THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

SURVEY OF THE LITERATURE ON IRRADIATION

Project 1108-34

Report One

A Progress Report

to

Rigid-When-Wet Technical Subcommittee

Fourdrinier Kraft Board Institute, Inc.

February 15, 1965

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IRRADIATION

INTRODUCTION

The irradiation of polymerizable and cross-linkable materials to form new paper-based products offers a fascinating potential to the paper industry. By comparison, our position on the use of irradiation as a processing tool is far more advanced than the state of development of the fuel cell, the plasma jet, the laser, and travel in space. However, extensive commercialization depends on further developments and economic factors (1-6). Most of the literature on irradiation reports studies based on low energy (Cobalt-60) sources using gamma rays of about 10,000 roentgens per hour. Newer high-voltage electron accelerators can put out 10,000 times this rate. This is greater than the difference between a gentle drizzle and a cloudburst.

The number of successful commercial applications for irradiation have been disappointingly few, despite the large amount of effort expended on interesting schemes for using irradiation for practical purposes. This may possibly be explained by the high investment costs, inexpert selection of materials for a given process, the need for better understanding of the controlling factors, and the recent development of more sophisticated irradiation devices. Also, for many of the suggested applications for irradiation processes cheaper solutions have been found using more conventional techniques.

It has been said that the present high cost of irradiation makes it necessary that it be used only in chain reactions (as in polymerization reactions), in high molecular weight compounds (where a large physical change results from a small chemical change), or in the production or treatment of expensive items. However, for some processes it was found that irradiation methods were cost saving

or there were no known alternatives to irradiation. The cross-linking of polyethylene film and wire coating, the sterilization of heat-sensitive pharmaceuticals, the production of ethyl bromide, and the preservation of food are good examples.

Interest has been shown in the possibility of using irradiation methods for polymerizing monomers which have been impregnated into wood to form a hard, dimensionally-more-stable, crack-resistant product which can be cut and sanded to make more useful furniture and formed items. A Cobalt-60 based pilot plant has been created for furthering the development of Novawood under Atomic Energy Commission auspices. This development of "Novawood" bears a strong similarity to the idea of treating paperboard with plastic materials to make it remain stiff when wet. The Novawood pilot plant experience should furnish useful information for other possible applications for irradiation techniques. Perhaps now is the time to consider a parallel project to develop a paper product impregnated with plastic and cured through irradiation with high voltage electrons.

Excellent books have been written on the subject of radiation by Robert O. Bolt, Frank A. Bovey and James G. Carroll, A. Charlesby, Adolph Chapiro, and A. J. Swallow (7-11).

RADIATION

Energy can be radiated either as electromagnetic waves or as energetic particles. The range of types of electromagnetic energy is apparent from Fig. 1 which spans the electromagnetic spectrum. We notice that the major categories include: radiowaves, heat or infrared rays, visible light, ultraviolet rays, x-rays, gamma rays, and cosmic rays. Some of the properties of various forms of electromagnetic energy are listed in Table I. Our current interest is centered largely on gamma radiation, which is a product of nuclear decay of radioactive

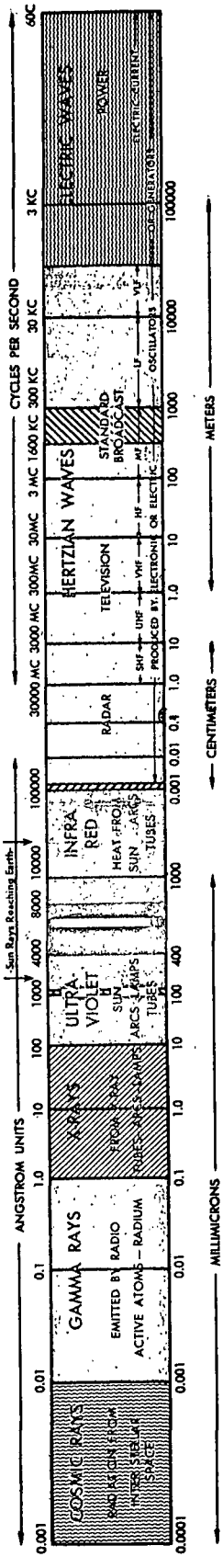

Figure 1. A Schematic Diagram of the Electromagnetic Spectrum

TABLE I

ELECTROMAGNETIC ENERGY

	Energy	Degree of Hazard	Penetration into Paper
X-rays			
1. Bremstrahlung		Low	Low
2. X-rays (machine produced)	30 Kv- Over 10 Mev	Hazardous	Very penetrating
3. Gamma rays (nuclear decay)	6-20 Mev	Hazardous	Very penetrating
Ultraviolet rays (plasma-jet)	50 Kw-	Low	Low
Visible light rays (plasma-jet)	2.6 Kw-	Low	Low
Visible light rays (laser)	--	Hazardous	Penetrating
Near infrared (plasma-jet)	100 Kw-	Low	--
Far infrared (laser)	--	Hazardous	--
Far infrared (plasma-jet)	--	--	--
Far infrared (laser)	--	--	--
Microwave (klystron)	50 megawatt-	Hazardous	Penetrating
Radio waves	--	None	Complete

elements and on high voltage electrons produced with various types of electron accelerators.

Particle energy in the form of electrons, positrons, protons, neutrons, and mesons can be considered radiation energy because the particles can be caused to move through significant distances if given the proper impetus.

The apparent mass of an electron varies with its velocity according to the equation $\underline{m} = \frac{\underline{m}_o}{(1 - \frac{\underline{v}}{\underline{c}})^{1/2}}$ where $\underline{c}$ is the speed of light.

The charge on the electron does not change with velocity according to relativistic theory.

Electrons may possess energy in the form of translational, rotational, and spin energy. The orbital electrons of an atom possess the latter two types of energy.

Electrons can interact with atoms and molecules to produce x-rays. The x-rays produced by low-voltage electrons are called Bremstrahlung after the German "glancing rays." The energy of the x-rays produced is equal to the loss of energy of the electrons as they are slowed down by the interaction with the electrical forces of the atoms. The very high-velocity electrons tend to take on wavelike properties of electromagnetic energy and the energy transitions are said to be "quantized."

SOURCES FOR RADIANT ENERGY

Gamma radiation, on the other hand, has been made commercially available largely from spent fuel rods which have been used in nuclear power plants or from radioactive isotopes manufactured by the Atomic Energy Commission. The spent fuel

element rods retain sufficient activity in the "cooling down period" to serve as useful sources for gamma irradiation.

The sale of radioactive cobalt and cesium isotopes in industrially interesting quantities by the Atomic Energy Commission makes these materials of possible interest for radiation processing. Cobalt-60 is produced by bombarding Cobalt-59 with neutrons from a nuclear reactor. Kilocurie sources are common today and the first megacurie source is now in operation.

The nuclear reactor itself may be considered as a powerful source for irradiation energy. The energy emitted as gamma rays and neutrons is about 10% of the total energy liberated in a reactor.

The use of fissiochemonuclear reactions has been suggested for chemical reactions such as the production of chemicals but little information is available. It is believed that specially designed nuclear reactors may someday be the source of radiation for industrial applications.

The penetrating nature of gamma rays makes them of interest for treating bulky materials. They could, theoretically at least, be used to treat reams and rolls of paper products.

Table II lists some of the better known forms of energetic particles. These include electrons, protons, neutrons, and ionized particles. Not included in this table are such particles as positrons, mesons, etc., which are known to exist but have been observed only in studies of nuclear reactions, etc.

It may be well to note that new developments such as the plasma devices have opened up new possibilities for using specific electromagnetic frequencies with far greater efficiency than ever before. However, these developments are in

TABLE II

ENERGETIC PARTICLES

	Energy	Half Life of Source	Radiation Hazard	Penetration into Paper	Power
Electrons					
Corona (silent discharge, "glow")	0.3 to 300 Kev	--	0 to slight	Few microns-?	?
Beta from Cobalt-60	306 Kev	5.3 years	Hazardous	0.15 cm.	?
Beta from Caesium-137	530 Kev	3.7 years	Hazardous	0.20 cm.	?
Beta from Caesium-134	561 Kev	2.3 years	Hazardous	0.20 cm.	?
Beta from Strontium-90	610 Mev		Hazardous	0.30 cm.	?
Transformer	? to 0.1 Mev	--	Low	0.05 cm.	?
Transformer, multiplying					
Insulating Core Transformer	0.3-1.0 Mev	--	Hazardous	0.15 to 0.5 cm.	10-20 Kw.
Resonant Transformer	0.1-3.5 Mev	--	Hazardous	0.05 to 1.8 cm.	5-28 Kw.
Dynamitron	0.25-6 Mev	--	Hazardous	0.13 to 3 cm.	5-30 Kw.
Capacitron	2 to 100 Mev	--	Hazardous	1 to 50 cm.	?
Van de Graaff (electrostatic)	0.3 to 6 Mev	--	Hazardous	0.15 to 3 cm.	0.5-3 Kw.
Linear Accelerator (Linac)	1.0 to 50 Mev	--	Hazardous	0.5 to 25 cm.	3-6 Kw.
Betatron	10 to 100 Mev	--	Hazardous	5 to 50 cm.	?
Cosmotron	Up to 3 Bev	--	Hazardous	?	?
Phasotron	25 Bev	--	Hazardous	?	?
Protons					
From nuclear reactor	?	--	Hazardous	?	?
From Bevatron	?	--	Hazardous	?	?
Alpha Particles					
From Radon	5.5 to 7.8 Mev	--	Hazardous	40 to 60 microns	?
From Polonium	5.3 Mev	--	Hazardous	35 microns	?
Neutrons					
From accelerators or reactors	1 to 50 Mev	10 min.	Hazardous	Many cm.	?
Ions					
From reactors or accelerators	100 Kev to 20 Mev	--	Hazardous	Low penetration	?

Note: The penetration into paper is taken as approximately the same as water. A more porous paper will show greater penetration.

such an early stage that a more extended discussion at this time is not possible.

Recent patents (12-14) relate to the use of relatively low-voltage or "glow-discharge" electrons for activating polymerizable substances in the vapor phase to produce organic protective coatings. Because of the low penetrating power of glow-discharge electrons the process must be carried out in a vacuum. Interfering positive ions present a problem if the process is to be used to coat paper. Most of the development work on this process has been in connection with coatings for metal containers. It is claimed that extremely thin protective coatings can be applied very economically.

Of more direct interest to the paper industry is the potential use of "high-voltage" electrons which permit irradiation of materials which do not need to be in a vacuum because of the penetrating power of the high-voltage electrons. Several types of electron accelerators are now being offered for industrial applications (Fig. 2). They can be roughly characterized as the Van de Graaff (electrostatic), Microwave, and Transformer types.

The Van de Graaff type (Fig. 3) builds up a high voltage by means of a power supply from which the electrons are transported by a belt to the top electrode. When a sufficient charge is built up the device discharges. The electrons are accelerated to high velocities by the potential difference which has been developed. The velocity of the electrons is sufficiently great to cause them to go through the thin metal window used to isolate the vacuum within the device from the pressure of the atmosphere. A three-million volt Van de Graaff with a 30-inch scanning width has been suggested for treating materials requiring greater penetration.

The linear microwave accelerator (Linac) carries electrons on the crest of a microwave to develop voltages of the order of 2 to 12 Mev (million electrovolts),

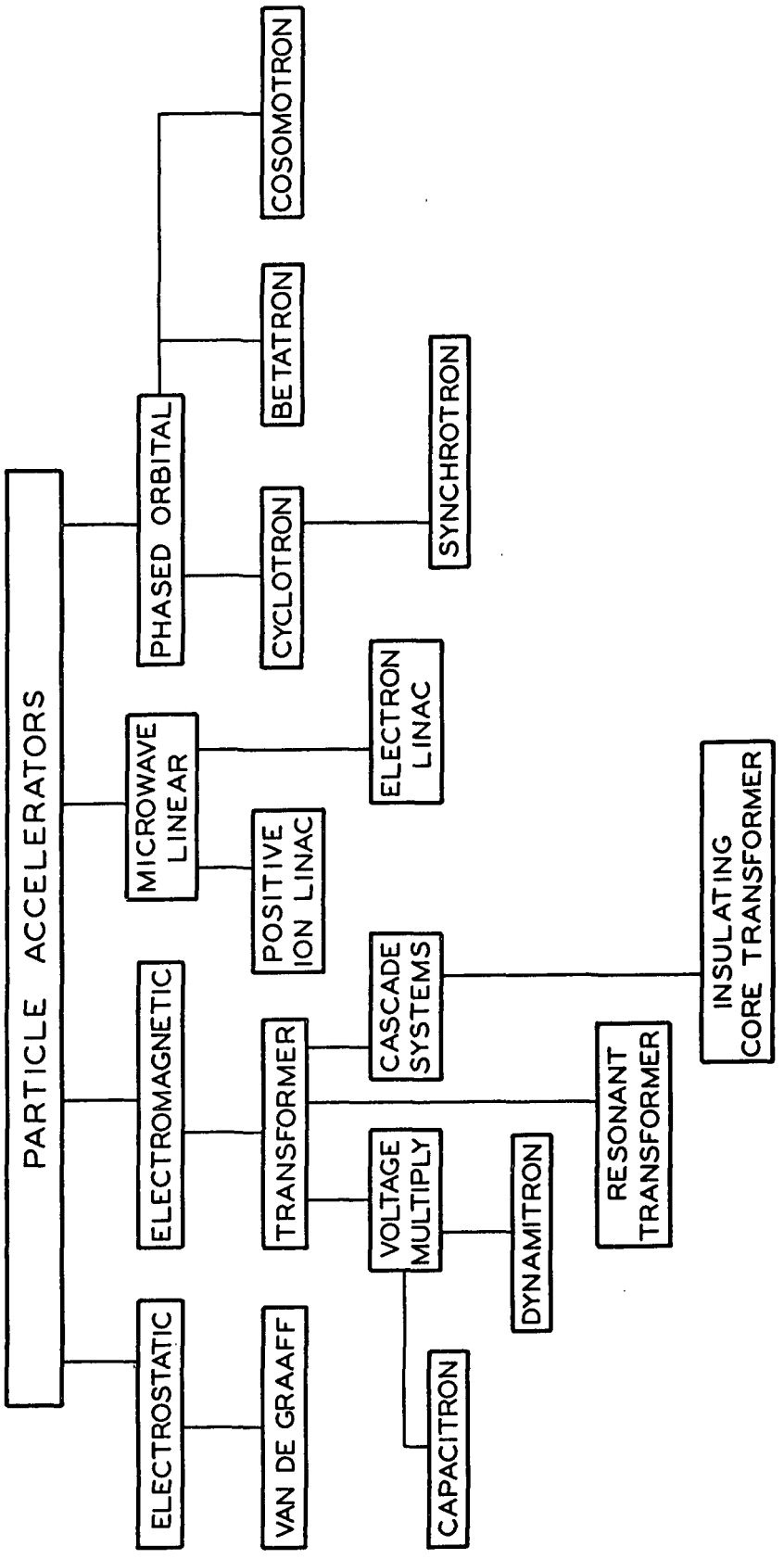

Figure 2. Particle Accelerators

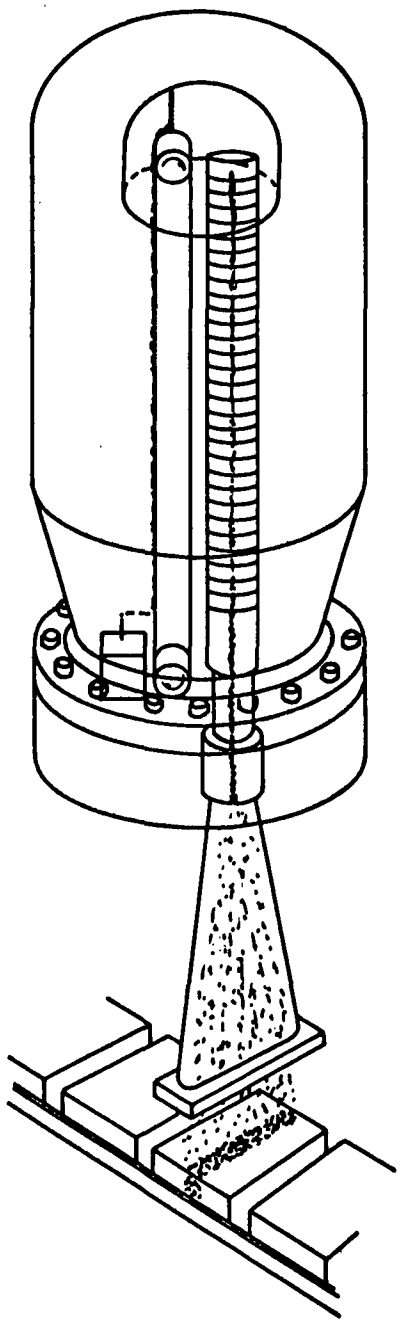

Figure.3. Van de Graaff Electron Accelerator

Fig. 4. The Linac and the Van de Graaff accelerators are produced by High Voltage Engineering Corporation.

The high voltage transformer type of accelerator is available as the "Insulating Core Transformer" (Fig. 5) sold by High Voltage Engineering Corporation. Figure 5 is a sketch of a cutaway of an insulating core transformer type of electron accelerator (ICT). The ICT power supply is a 3-phase power transformer with multiple secondary windings, each of which is insulated from the other. Each section of the magnetic core is also insulated with a layer of plastic. The alternating current in each secondary is rectified and the DC outputs are connected in series. The electrostatic and electromagnetic fields thus exist in the same space since the individual secondary windings are stacked on the primary winding.

The DC current leaves the power supply through a cable to the top of the electron accelerator system. This system consists of a high voltage terminal, an accelerator tube, and a steel pressure tank. The electrons introduced from the cathode in this section are accelerated to the scanner.

The electron beam is then electromagnetically scanned at many cycles per second over a distance of 48 inches, the width of the beam being only a few tenths of an inch. Several accelerator heads and scanners can be used with one power supply to permit the irradiation of wider sheets, or to permit irradiation from both sides or two or three different lines.

The "Resonant Transformer" of the General Electric Corporation and the "Dynamitron" of Radiation Dynamics Incorporated are also transformer-type electron accelerators. The electrons do not have the penetrating power of gamma rays from radioactive isotopes but the fact that they are furnished in a copious supply with

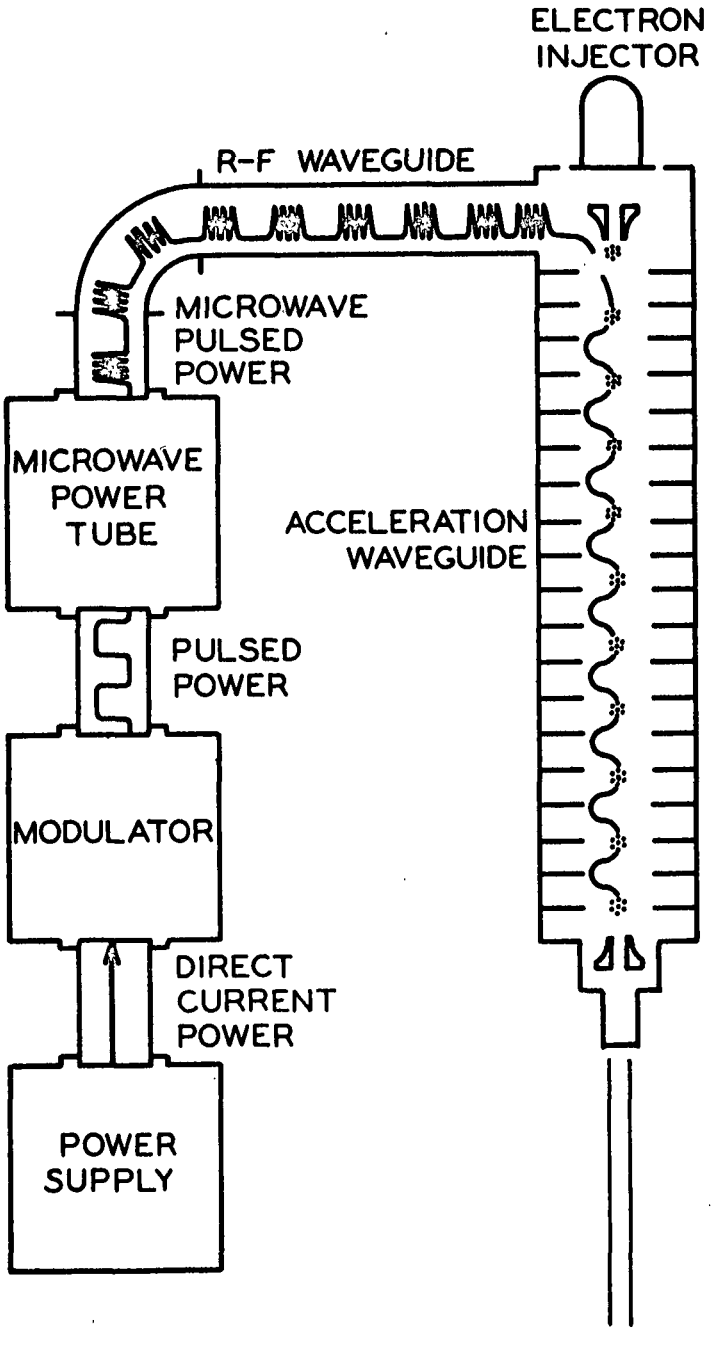

Figure 4. "Linac" (Linear Microwave Accelerator)

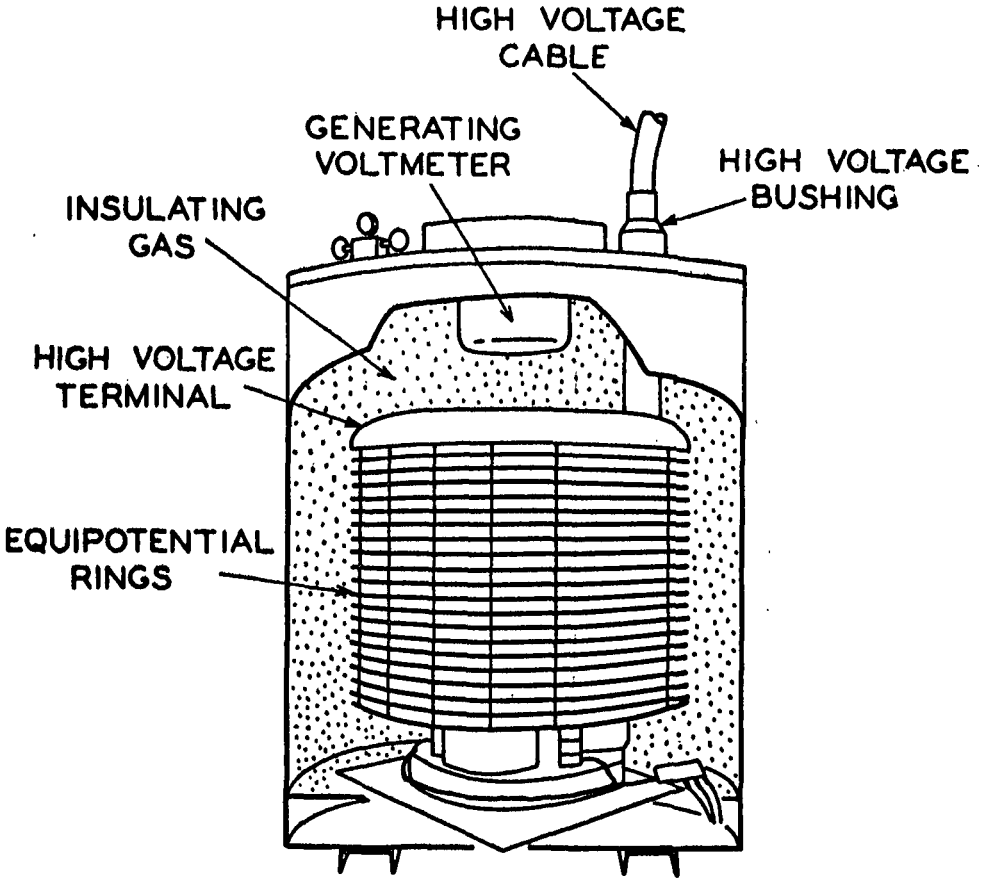

Figure 5. ICT (Insulating Core Transformer)

sufficient energy to penetrate most paper products should make transformer-type electron accelerators especially attractive to the paper industry.

Web widths up to 48 inches can be treated because the electron beam coming out of the accelerator is made to traverse the width of the product being irradiated. This "scanning" process is caused by the interaction of the electron beam with the electromagnetic field produced by a set of coils causing the electron beam to be deflected at a rate which can be controlled within certain limits. This action is somewhat similar to the action of the electron beam in a television picture tube in which the vertical oscillator has failed. There we see only a single bright line formed by the electrons sprayed across the width of the screen.

A schematic of the layout for electron beam irradiation of paper products is pictured in Fig. 6.

Other types of accelerators have been developed which use the accelerating power of a high-frequency oscillator output voltage acting in phase on the electron beam which is held in a circular path. The voltage developed by such devices as the betatron, cyclotron, and synchrotron are generally higher than necessary for most industrial chemical processing. Also they are large in size, making them cumbersome and difficult to fit into a plant operation. The size of an accelerator becomes important as the required voltage goes above 1 Mev. Table III gives some of the physical sizes of commercial electron accelerators for different output voltages.

Figure 7 shows the overlapping capabilities of the different classes of electron accelerators.

The silent discharge includes a number of types, such as the Ozonizer, Semi-corona, Corona, Glow, Discharge, and Electrodeless discharge.

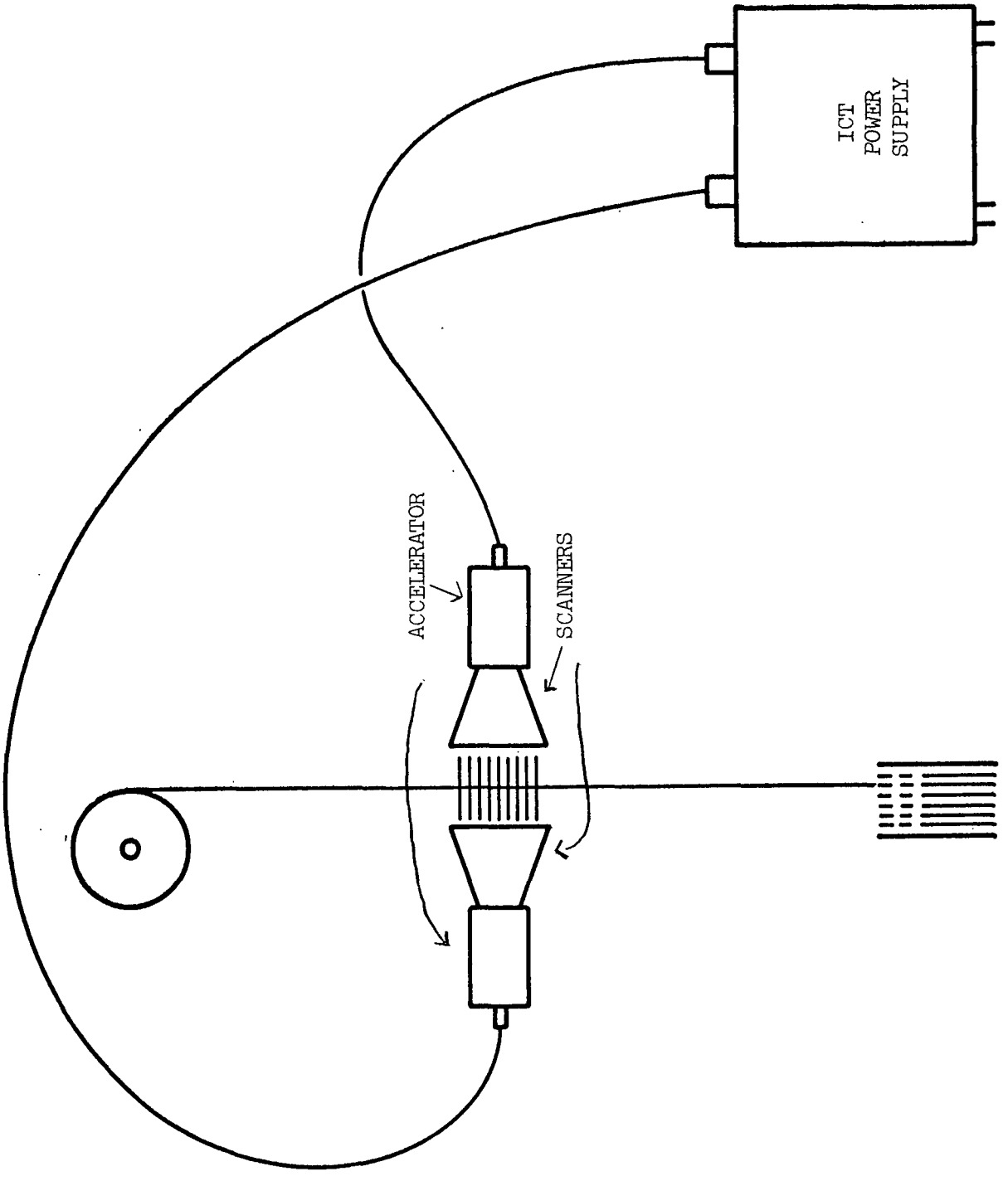

Figure 6. Schematic for Radiation Processing of Paper

TABLE III

SIZE OF ELECTRON ACCELERATORS

Voltage	Size
0.25 – 0.5 Mev.	8 feet long, 4 feet diameter
0.5 – 1.0 Mev.	8 feet long, 4 feet diameter
0.75 – 1.5 Mev.	11 feet long, 4 feet diameter
1.0 – 2.0 Mev.	15 feet long, 6 feet diameter
1.5 – 3.0 Mev.	20 feet long, 6 feet diameter
1.0 – 6.0 Mev.	33 feet long, 10 feet diameter

Note: These are based on the "Dynamitron" dimensions.

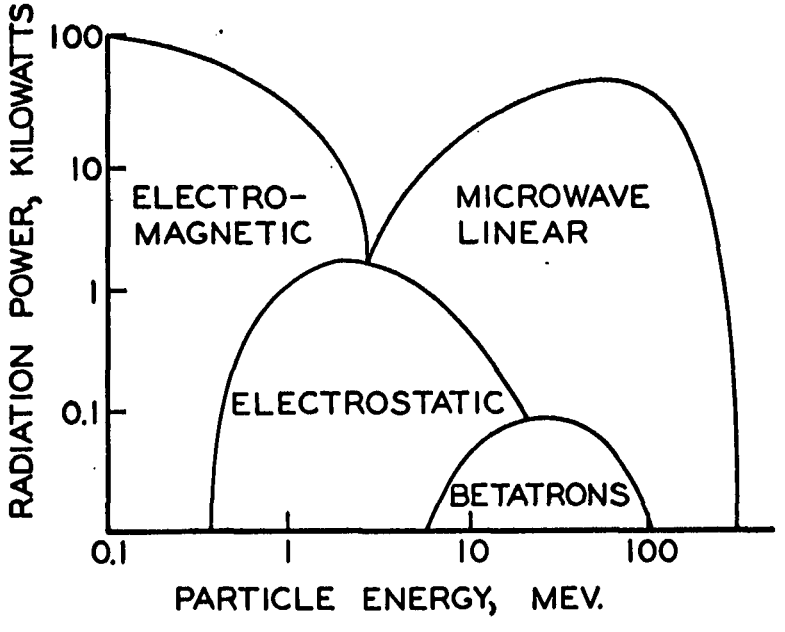

Figure 7. Approximate Power and Voltage Range of Electron Accelerator

Radiation at high intensity at controlled wavelengths is available through the development of the plasma jet. The plasma jet is essentially a controlled electric arc contained in a transparent cylinder containing certain types of gas. One prototype unit has been operated for a short time at an input of 100 kw. The limit of power input is not known at the present time. At 50 kw. input the plasma arc has produced over 15 kw. of radiant energy. The wavelengths of the radiation can be changed at will by changing the type of gas used to surround the arc.

A new device which produces light-activated radiation (laser) is still in its infancy. Its usefulness is being explored and the first reported use has been in medicine where difficult, if not formerly impossible, eye operations are now achieved with a laser. Its power has been demonstrated by melting heavy chains in seconds.

The disruptive charges, the arc and the spark, are much more violent in nature than the silent discharge. In general, the results are so drastic that almost every possible atom or radical is affected by the discharge. It is at present impossible to control the outcome of such a process if used with polymers and most monomers.

INTERACTION OF RADIATION WITH MATTER

GAMMA RAYS

When gamma rays are caused to impinge on a material their energy is usually dissipated through the absorption of the rays by the material and by scattering. The portion of the energy that is absorbed may induce the release of energetic secondary electrons. This interaction with the orbital electrons is called a "photoelectric effect" or the "Compton effect." The probability of

photoelectric absorption increases rapidly both with the wavelength of the radiation and with the atomic number of the irradiated medium. The probability of this process is proportional to $\lambda^{Q} Z^{Q}$. For most organic compounds and plastics the photoelectric process becomes important only below 0.2 Mev.

In the case of more energetic gamma radiation a large portion of the energy is dissipated through a process wherein only a fraction of the energy is transferred to an electron. The residual energy emerges from the zone of interaction with a longer wavelength and at an angle with the incident path.

For electromagnetic radiation having quantum energies in excess of 1.02 Mev., a fraction of the radiation energy is absorbed with the resultant production of electron pairs. In this process, the photon is changed into a negatron plus a positron of equal energy values. Thus, we find that when electromagnetic energy (gamma radiation) goes through matter the absorbed energy is converted into fast-moving electrons and short-lived positrons.

Since the final effect will most likely be the same for gamma irradiation and irradiation with high energy electrons (because secondary electrons are the first phase of a gamma irradiation) we may cover both by referring only to electron irradiation, with the understanding that it refers to either of these types except as far as penetration and requirements for shielding, etc. are required.

ELECTRONS

An electron from an accelerator may have about a million times the energy of a typical chemical bond, a hundred thousand times the energy required to ionize molecules. There is no doubt that in many cases atoms and radicals are formed by the decomposition of organic or inorganic compounds.

The size of an electron is very small. By applying the relativity relationship, $E = MC^2$, and the energy equivalent, $E = e^2R$ it can be calculated that the radius of an electron is 2.8×10^{-13} centimeter. There is no wonder that a 1 Mev. electron will ionize only about 1 in 2,500 of the molecules it traverses.

Another interesting observation is that when a parallel beam of fast electrons enters a solid or liquid medium the energy absorbed per gram of medium may be greater as the beam penetrates into the substance. This effect is due to the scattering of the initially parallel beam.

As the electron slows down it becomes more efficient at ionization because it remains longer near each atom and the "linear energy transfer" (LET) goes up. The LET is usually expressed in kev. per micron of path.

Electrostatic attraction will cause a sudden change in the trajectory of an electron if it passes close to an atomic nucleus. Owing to the considerable difference in the masses involved, very little energy is transmitted to the nucleus, however, and the collision may be referred to as elastic. The maximum energy which can be transferred to a nucleus of mass M by an electron of energy Mev. is approximately $E_{max} = 2{,}200\ E\ (1 + E)/M$ where E_{max} is expressed in ev.; thus, a 100 kev. electron colliding with a hydrogen atom can impart to it a maximum of 240 ev., while for a carbon atom the maximum energy transfer is about 20 ev., or sufficient energy to break most organic chemical bonds.

The number of close collisions is in any case small, and the main effect of electron-nucleus interaction is the scattering it causes in the incident beam.

For most plastic materials, energy loss due to back scatter need only be taken into account in the most accurate measurements. Owing to multiple scattering

caused by electron-nuclear reaction the depth of penetration of an electron into a specimen differs from the true range (or track length measured along its path).

The types of materials which may come under consideration for irradiation processes are too numerous to consider here. However, it may be well to briefly review the effects of radiation on monomers, prepolymers, and polymers (with special note on cellulose).

Energetic electrons may be able to react in several ways with molecules during the course of their passage through materials. The relatively simple oxygen molecules can end up as 11 different particles. The more important reactions include: simple electron attachment, dissociative electron capture and ion-electron combination. The new ionic or excited particles then react with each other in a number of possible ways. By far the most important are the free radicals which are formed as a result of a dissociation of excited molecules. Table IV lists the minimum energy requirements to ionize various neutral molecules. The values fall between 7.2 electron volts for the tertiary butyl radical and 17.8 electron volts to ionize the fluorine molecule.

The ionization of gas molecules is utilized in neon signs and fluorescent lights. Here the ionized gas carries the current and gives off the visible light. If organic molecules are included in the gas at low pressure and subjected to an electrical potential of the right magnitude they can be fragmented and put into "excited" states and chemical reactions can be caused to take place. This knowledge is put to use in the "Glow Discharge" process. The patents previously mentioned describe the formation of organic polymer coatings by such a technique. This is carried out at a pressure of about 1.5×10^{-4} Torr. (The unit Torr equals the pressure of 1 millimeter of mercury at 0°C. and standard gravity). It is said that, when using paper as a substrate for this process, higher frequencies must be

TABLE IV

MINIMUM ENERGY TO IONIZE MOLECULES

Molecule	Electron Volts (ev.)
CH_3I	9.1
NO	9.5
I_2	9.7
CH_3Br	10.0
CS_2	10.4
H_2S	10.42
CS	10.6
CH_3C	10.7
S_2	10.7
NO_2	11.0
O_2	12.2
H_2O	12.6
HI	12.8
Br_2	12.8
N_2O	12.9
SO_2	13.1
Cl_2	13.2
HBr	13.2
CO_2	13.8
HCl	13.8
CN	14.0
CO	14.1
H_2	15.4
N_2	15.6
HF	17.7
F_2	17.8

Minimum Energy to Ionize Hydrocarbon Molecules and Radicals

Hydrocarbon Molecules	Energy, ev.
Toluene	8.9
Butadiene	9.1
Benzene	9.2
Isobutylene	9.65
Propylene	9.7
n-butane	10.3
Ethylene	10.5
Propane	11.3
Acetylene	11.4
Ethane	11.6
Methane	13.1
Radicals	
Tertiary butyl	7.2
Isopropyl	7.8
n-propyl	7.8
Ethyl	8.7
Methyl	10.1

used to overcome the capacitative reactance of the paper. Electrons can be emitted by the paper under the bombardment by positive ions producing reactive sites in the paper itself. For this reason, coatings formed on paper tend to be chemically bound to the paper, it is believed. It is claimed that fluorinated polymer coatings can be applied by this process whereas the application of such coatings is practically impossible by conventional methods. Another reason for the interest in this process is the economy of the starting materials and the elimination of solvent and drying steps. Another interesting consideration is that the thickness of the coating is regulated because of the increasing impedance (opposition to flow of alternating current) of the polymer with thickness of the deposit. Another advantage claimed is that the process does not require the high voltages used in electron accelerators and therefore the equipment cost should be much lower. One of the disadvantages, of course, is that the process must be carried out in a vacuum or at reduced pressures of the order of 250 microns (mercury) or better.

The attachment of an electron directly to a neutral molecule is believed to take place only in the case of slow-moving electrons. Also, it is concluded that this process occurs only with molecules which have what are virtually free valences (e.g. orbital angular moments or uncoupled spin). The electron which joins a molecule will process or spin at a different frequency. Diatomic molecules with symmetrical structure and highly symmetrical polyatomic molecules show little tendency to capture electrons. Oxygen, however, is a diatomic molecule which can act as an efficient electron trap because of its two unpaired electrons.

If a substance having a low affinity for electrons contains a contaminant of high electron affinity, this impurity may capture most slow electrons and affect a desired radiation-chemical process yield adversely.

Some materials on being irradiated will dissociate to form two or more new particles from each molecule whose binding energy is less than the energy of the captured electron. In such dissociative processes one of the products may be a free radical and the other a free radical ion.

When a low velocity electron comes in the vicinity of a positive ion, combination occurs because of the strong coulombic interaction with the formation of an excited molecule. $AB^{+} + e \longrightarrow AB^{*}$

The excitation energy may be as great as 10 to 15 ev. which is sufficient to cause the molecule to undergo dissociation and a permanent chemical change results.

Other reactions which can take place as a result of irradiation are interactions between positive and negative ions to form excited molecules and interactions between ions and molecules.

Free radical formation is probably the most important consideration when irradiation is used for polymerizable or cross-linking systems.

Another type of reaction which may be very important is "energy transfer" which may take place with "charge transfer" or "excitation transfer." Thus, $A^{+} + B \longrightarrow A + B^{+}$ and $A^{*} + B \longrightarrow A + B^{*}$.

Transfer reactions may be important when mixtures of monomers are to be used in irradiation polymerization. Activation energies have been established for only a few transfer reactions. More basic research would be most helpful in clarifying the complicated kinetics of radiation polymerization.

Extensive studies of the effect of radiation on polymers indicate that polymers may be either degraded or cross-linked on irradiation. Actually, it is

possible that both processes are going on simultaneously in some polymers, however, the ultimate effect is caused by the relative rates of these reactions. One of the first commercial uses for irradiation was for the cross-linking of polyethylene to produce a shrinkable polymer. Such a product has found use in wire coatings and for packaging film. In general, materials like polytetrafluoroethylene, polymethacrylate, and polyvinylidene chloride are degraded by radiation. Polyethylene, polystyrene, polyvinyl fluoride and polyvinyl alcohol are found to cross-link when irradiated with gamma rays or with high velocity electrons.

There are a number of considerations that affect the efficiency of an irradiation process. For example, when irradiation of a monomer is carried out in the presence of certain solvents, the radicals produced in the solvent may initiate further polymerization. The size of a molecule, or more correctly its cross-sectional area, may affect the efficiency with which the electrons are captured. The cross-section area is often expressed in barns where a barn is the unit of area that equals 10^{-24} square centimeters.

EFFECT ON CELLULOSE

Irradiation of cellulose offers at least six possibilities for forming new products — oxidation cleavage, degradation, cross linking, substitution, and grafting. Irradiation of treated papers offers new avenues for sizing and impregnation.

Cellulose is relatively sensitive to the effect of radiation but still sufficiently resistant for paper to be used in a radiation process where the level of radiation required is within the tolerance for paper.

The intrinsic viscosity falls off as a function of the radiation dose $\underline{D}$ according to the formula $\log [\eta] = -\underline{a} \log (\underline{D} + \underline{D}_o) + \underline{C}$ where $\underline{a}$ is the exponent

of $\bar{M}_n$ in the Mark-Houwink equation, $[\eta] = k\bar{M}_n^a$, and D_o is the dose that would be required to degrade a polymer molecule of infinite length to a polymer having the same $\bar{M}_n$ as the initial polymer (10).

The fibrous nature of cotton cellulose disintegrates at gamma ray doses higher than 5-10 million roentgen.

After 10^7 rads a 35-lb. (per 1000 sq. ft.) kraft paper with 10 lb. (per 1000 sq. ft.) of polyethylene coating showed a decrease of about 20% in tensile strength and about 10% decrease in internal tear. The sealing strength (peel) dropped about 25% (7).

The type and amount of various reaction products formed by ionizing radiation action on cellulose will depend on many things including type of wood, amount of moisture, the intensity of the irradiation, the presence or absence of oxygen and other gases as well as the presence or absence of fillers, sizing, and various additives.

Some of the possible reactions as mentioned in the literature include the formation of carbonyl and carboxyl groups.

Gas formation is generally noticed and is attributed to the detachment of hydrogen from C-2, C-3, or C-6 of a glucose unit. Smaller amounts of CO, CO_2, and CH_3 have been found (16-19).

Studies using electron paramagnetic spin resonance (EPR) techniques indicate the formation of free radicals. Stored irradiated specimens of purified cellulose do not suffer appreciable decay of free electrons in several days. Different radicals appear to have differing lifetimes.

Cross linking of nonionic water-soluble cellulose derivatives has been studied. Gelation has been reported occurring very rapidly after total doses of 0.25 Mrad in very dilute aqueous solutions.

Oxidation of the cellulose and cleavage of the 1,4-β-glucosyl units are believed to be the principal reactions that cotton cellulose undergoes on irradiation with high energy gamma radiation.

Radiation-induced graft polymers of cellulose have been studied by many workers. The types of monomers which have been grafted to cellulose include styrene, acrylonitrile butadiene, vinyl chloride, methyl methacrylate, methacrylic amide, and vinyl acetate. Despite apparently extensive grafting, and homopolymer formation, only one in 5000 to 10,000 anhydroglucose units or one in 10 to 20 cellulose chains carried a grafted polystyrene chain (20).

Grafting is claimed to increase the thermostability, resistance to micro-organisms, its dyeability, and adhesion capacity of cellulose without seriously affecting its strength properties. The heat of wetting and the moisture equilibrium characteristics variation can be either positive or negative depending on the chemical nature of the grafted monomers, (21-22).

INHIBITORS

Certain materials have been found to act as inhibitors or "antirads" when added to polymerizable monomers which are liquid. It has been observed that some of these materials do not function when the polymerizable material is in the solid state. This is believed to take place because in the liquid state the process is a free radical mechanism and in the solid state it is ionic. The materials listed in Table V have been mentioned as inhibitors for polymerization reactions.

TABLE V

INHIBITORS

1,1-diphenyl-2-picryl-hydrazyl
pyridine
2-hydroxy-3-tertiary-5-ethylphenylmethane
pyrogallol
oxygen
benzoquinone
iodine
2,2-diphenyl-1-picrylhydrazyl
p-$O_2NC_6H_4OH$
4-nitroso-1-naphthol
$CHCl_3$
CCl_4
benzene

Note: The above information is collected from a number of sources (23-26).

RADIATION DOSAGE

In radiation processing there may be a large difference between the amount of radiation impinging upon a substance being irradiated and the actual amount of energy absorbed by the material. It is important to note the difference in the two ways of characterizing the level of radiation energy. One of the more frustrating aspects of the literature on radiation processing is due to the varied terminology. Radiation treatments are quoted in roentgens, electron volts, reps, rems, and rads. The reason for this varied terminology may be understood when it is recognized that radiation may stem from radioactive materials or from electron accelerator devices. We encounter units of radioactivity which express the rate at which the nuclei or radioactive elements disintegrate and units of radiation intensity which express the rate of emission or flux density.

The commonly accepted unit of radioactivity is the curie. It is now defined as the quantity of any radioactive element which undergoes 3.700×10^{10} disintegrations per second. With the recent development of very powerful artificial sources, the kilocurie (3.700×10^{13} disintegrations/second) has become a useful unit.

In most cases we are concerned with the amount of radiation absorbed and it is very hazardous to estimate this quantity from the radiation emitted unless this particular quantity has been measured previously for the material being irradiated. The total amount of radiation absorbed is often called the "dose," a term which stems from the medical application for irradiation. Thus, the "dose" is the absorbed radiation flux integrated over the period of irradiation.

The unit of x-ray and gamma ray dose is the roentgen (r.) which is defined as the quantity of x-ray or gamma-ray radiation such that the associated corpuscular emission per 0.001293 gram of air (i.e., 1 $cm.^3$ of air at S.T.P.) produces, in air, ions carrying 1 e.s.u. of electricity of either sign. The roentgen is equivalent to the absorption of 83 ergs per gram of air or about 93 ergs per gram of water. Again it is important to note that this expresses the energy that a standard would have received instead of the energy a sample actually received.

The energy W required to form one ion pair in air is 32.5 electron volts for x-rays and gamma rays.

The "rad" is a unit which has been chosen to express absorbed dose and is defined by the International Commission on Radiological Units as 100 ergs (absorbed) per gram of material. This single unit is sufficient for all types of radiation. The rad now displaces the older "rep" which stemmed from "roentgen equivalent physical" and which was defined as the quantity of radiation either

electromagnetic or particulate, which upon absorption in 1 gram of body tissue or of water (nearly equivalent) releases the same amount of energy as 1 roentgen of x-ray or gamma radiation and the "rem" which stems from "roentgen equivalent man" and which is defined as the quantity of radiation of any kind producing biological damage in man equivalent to that caused by one roentgen of x-radiation or gamma radiation. Table VI lists the various units used for expressing the amount of high energy radiation.

Table VII gives the conversion factors for various radiation units useful in translating the writings of earlier workers in the field and for calculations relating to physical effects of irradiation.

Figure 8 shows the relative effects of radiation on various materials as a function of the dose. Many schemes have been devised for measuring the dose absorbed by materials undergoing irradiation. The doses employed are usually so large that photographic methods, scintillation counters, and ionization chambers are impractical. The methods that have been found useful include calorimetric techniques which measure the temperature rise of water or aluminum. A commonly used method is the color change that takes place when cobalt glass or layers of dyed cellophane are placed in the path of the radiant energy. Chemical dosimeters such as those based on the oxidation of ferrous sulfate have been used for gamma radiation work. By calibration against ionization chambers it appears that about 15.5 to 20 atoms of iron are oxidized per 100 ev. absorbed. This technique has been used extensively at the Argonne Laboratories. The electron volt (ev.), is a convenient unit of energy when used in connection with accelerators and is defined as the energy acquired by a single electron (charge 1.602×10^{-19}/coulombs) falling through a potential difference of 1 volt. Various equivalents for the electron volt are given in Table VIII.

TABLE VI

TERMS USED IN HIGH ENERGY RADIATION

Specific activity	The amount of radioactive isotope present per unit weight of the total element. Usually expressed in curies or millicuries per gram.
Curie	The quantity of radioactive material giving 3.700×10^{10} disintegrations per second.
W	The energy required to form 1 ion-pair in air. This is 32.5 electron volts (ev.) for x-rays and gamma rays and 35 ev. for heavy particles.
Roentgen, r.	Produces 1 e.s.u. of charge in 1 $cm.^3$ (0.001293 g.) of air at zero degrees centigrade and 760 millimeters, or 2.1×10^9 ion pairs. Equivalent to absorption of 83 ergs per gram of air or about 93 ergs per gram of water and many organic molecules.
rhm	The abbreviation for 1 roentgen per hour at 1 meter.
rep (roentgen equivalent physical)	The quantity of radiation of any kind producing 83 ergs per gram of body tissue of water.
megarep	10^6 rep
rad (short for radiation)	The quantity of radiation of any kind producing 100 ergs per gram of the absorber concerned.
megarad	10^6 rad.
rem. (roentgen equivalent man)	The quantity of radiation of any kind producing biological damage in man equivalent to that caused by 1 r. of x-radiation or gamma-radiation.
1 pile unit	Exposure to 10^{17} thermoneutrons per square centimeter plus associated gamma rays and fast neutrons.
Megawatt-days per central ton (M.w.d./c.t.)	Equivalent to 3×10^{17} nvt.

TABLE VII

RADIATION TERM CONVERSION CHART

From	To	Multiplier
Rads	ergs per gram	100
Rad (tissue)	ergs per gram	90.9
Rad (water)	ergs per gram	90
Rads (per hour)	neutrons per $cm.^2/sec.$	8.3×10^4
ev per gram	ergs per gram	1.6×10^{-12}
Total dose of thermal neutrons	rads per hour	4.2×10^{-6}
Rem	rad (tissue)	91.29
Rem per hour	neutrons per $cm.^2/sec.$	8.3×10^3
$Mev/cm.^2$	ergs per gram	4.5×10^{-8}
$Photons/cm.^2$	ergs per gram	4.5×10^{-8}
$Photons/cm.^2$	rep	5×10^{-10}
Roentgen	rad (tissue)	1.036
Roentgen	ergs per gram	87.7
Rep	rad (tissue)	1.074
Rep	ergs per gram	84.6
rep/hour	neutrons per $cm.^2/sec.$	7.1×10^4
Kilocalories	electron volts	0.208

Note: Adapted after a chart by Henning H. Lind Olesen (27).

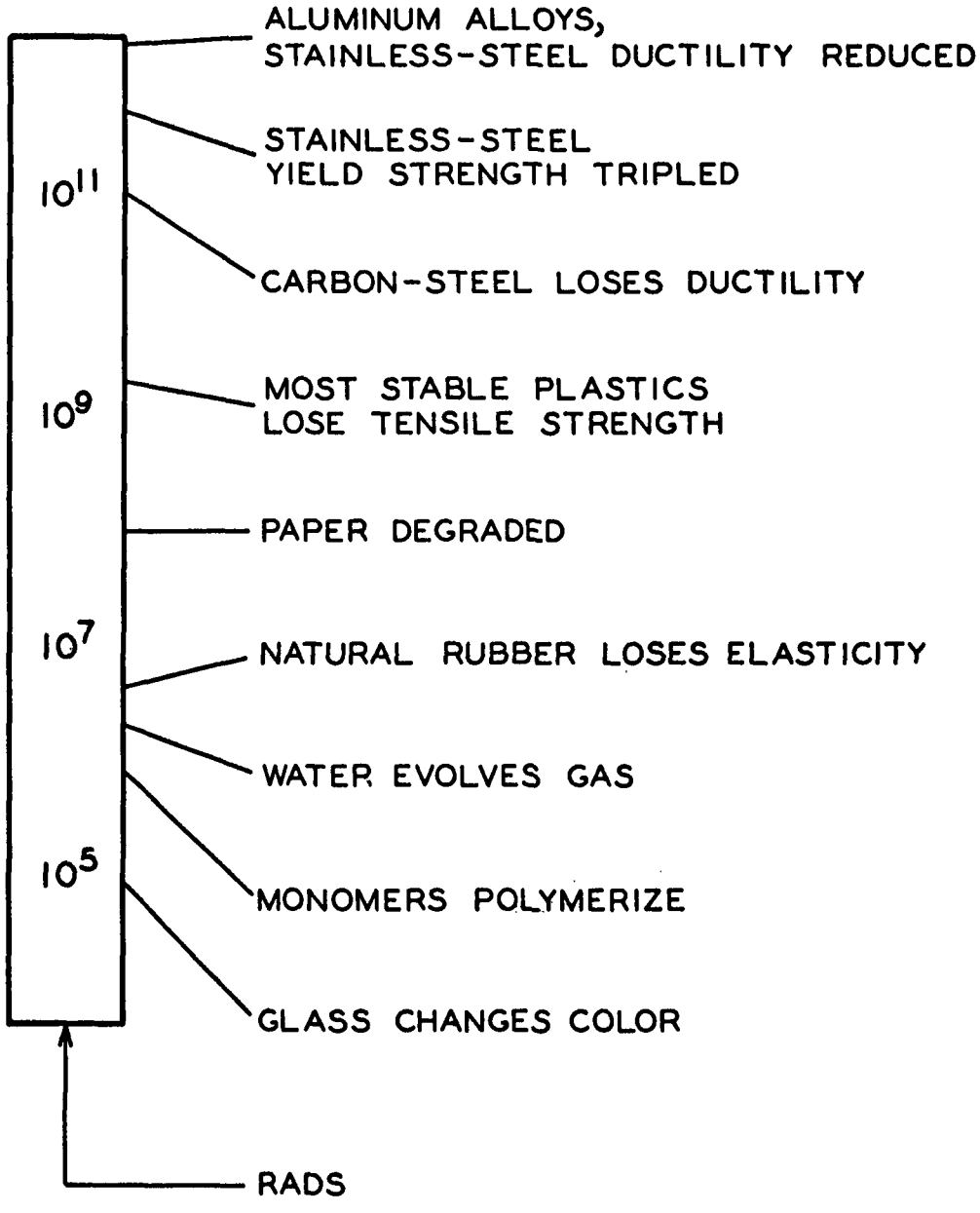

Figure 8. Effect of Radiation on Various Materials

TABLE VIII

THE ELECTRON VOLT AND ITS EQUIVALENTS

1 electron volt, ev. $= 1.602 \times 10^{-12}$ erg
$= 1.602 \times 10^{-19}$ joule
$= 3.828 \times 10^{-20}$ calorie
$= 1.602 \times 10^{-20}$ gram-megarad
$= 4.450 \times 10^{-26}$ kwh.

In a reactor output the energy absorbed from gamma rays corresponds to a gamma flux of about 50% of the thermoflux. At 10^{12} thermoflux this is equivalent to about 10^{6} roentgens per hour.

The sensitivity of a system to radiation can be expressed in terms of the number of changes produced by a given radiation dose. The yield is usually expressed in terms of a "G" value, this being defined as the number of changes of a given kind produced per 100 ev. absorbed. In using G values it is not implied that all the energy absorbed is used to produce the relevant entities. This definition has the advantage that no assumptions are made as to the mechanisms of the reaction, and for any system different G values can be given to denote each of a series of products formed in the course of a single irradiation. Thus, in selecting materials for a given polymerization application one of the most important considerations in selecting monomers other than the physical properties required of the polymer is the G value of the monomer. The higher the G value therefore the more efficient will be the polymerization process. Unfortunately, this value is not at the present time available in the literature for many materials which are of potential interest for use in treating paper. Each substance has a very specific sensitivity to radiation and this can vary quite widely. For example, the initial "G" value for dry cellulose suffering a cleavage of radicals is 2.8 while the main chain scission of cellulose has been given a G value of 10.0

(18,19). Table IX gives some of the G values for the polymerization of various monomers. The G values for different sources may vary depending upon the method used in dosimetry. In noting the G values for benzene, toluene, and styrene we may assume that these chemicals are radiation resistant whereas we find high values for halogenated aliphatics like carbon tetrachloride, chloroform, bromoform, etc. Halogenated aromatics have G values more comparable to aliphatic hydrocarbons than to the aromatics. Differences in polymerization kinetics may account for differences in observed G values. Table IX gives some of the experimental G values reported in the literature for monomer polymerization (28-33).

"G" values can be in the tens of thousands for reactions that are exothermic and which can propagate as a chain reaction once initialed by radiation. Such high G value systems are especially likely to be successful commercially.

Since a rad is a unit of energy absorbed per unit weight of material over any time interval, it can be expressed as 1.26×10^{-6} watt hours per pound. Since the weight of product formed is directly proportional to the G value and the molecular weight, we may set up an expression relating the energy requirements in terms of G value and molecular weight, $e = \frac{1.22 \times 10^{3}}{G(MW)}$ x kwh./lb. as suggested by Kircher and Jeffrey (3).

Considerable work has been done in studying the grafting of monomers to various polymers (including cellulose) using high energy radiation. Grafting with styrene has been carried out by irradiating the cellulose immersed in the monomer and also by irradiating the cellulose and then immersing it in the styrene. Better control of grafting is possible when the cellulose is first preswollen with a polar swelling agent such as water, formamide, formic acid, or dimethyl sulfoxide (44).

TABLE IX

G VALUES

Various Monomers	
Isobutylene/ZnO	0.16 to 2 x 10^6 (with high surface ZnO)
Styrene	.22 to .97
Acrylonitrile	2.4 to 5.0
Methyl methacrylate	5.5 to 11.5
Vinyl acetate	9 to 12
Methyl cyanide	10 to 50
Propargyl alcohol	10 to 50
Propargyl bromide	10 to 50
Phenyl acetylene	10 to 50
Allyl acetate	70
Allyl bromide	95
Allyl chloride	480
Ethylene + comonomer	640 to 20,000 (depending upon comonomer)
Irradiation of Polymers	
Cellulose	2.8 to 13.5 (with moisture content)
Polyvinyl alcohol	0.2 to 0.6 (main chain scission) 2. (production of carbonyl groups)
Polyvinyl chloride (in solvent)	2.15 (cross linking)
Polyvinyl chloride	5.4 in air (degradation) [25 in water (crosslinks)]
Polyethylene (molten)	50.6 (cross linking)
Polybutadiene (in halogenated H.C.S.)	2.4 to 9.74 (cis-trans isomerization)
Polypropylene after 12 megarad	1.3 (cross link)
Polypropylene at low doses	4.95 (scission)
Polyethylene	2.4 to 2.8 at 77°k (radical formation) (cross linking)
Polyethylene (linear)	50.6 (vinylene decay postulated)
Polystyrene	0.8 (gas evolves)
Poly (α-methylstyrene)	0.035 H_2 formation 0.003 CH_4 formation 0.0025 2-butene formation 0.25 (chain scission)(in vacuum) 0.08 bond scission in O_2 0.16 bond scission in air
Rubber	0.9 (cross linking)(in vacuum)
Polydimethyl siloxane	2.2-2.5 cross linking

Acrylonitrile has been grafted to filter paper to give a strengthened product. In the absence of water no grafting was observed (45).

According to tests with mixtures of monomers, the graft polymerization effects are strongly dependent on the composition of each comonomer mixture. Mixtures which were tried include butadiene-styrene, butadiene-acrylonitrile, and styrene-acrylonitrile. Another study found that the grafted celluloses contain large amounts of ungrafted cellulose and homopolymer. This can lead to disappointing properties compared to those of isolated graft copolymers. Much more work is needed on the properties of grafted products prepared under different conditions before conclusions can be drawn regarding the practical value of grafted cellulosic materials (46). It appears that in most cases reported there is one grafted chain for every 20 glucose residues. Grafting of monomers to cellulose is claimed to result in a change in the heat of wetting with water as well as its water-vapor absorption capacity. Cellulose grafted with acrylonitrile by irradiation is more resistant to microbiol action and sunlight. It can be dyed better than the original materials (47).

Irradiation of dilute (4%) aqueous solutions of methyl cellulose with 2.1 Mrad at 4.5 Mrad/min. caused bond formation and an increase in molecular weight according to Hillend (48).

Snell formed polymers from glucose by irradiating a 1% aqueous solution (49).

BEAM PENETRATION

Gamma radiation is very penetrating and careful shielding is necessary to protect workers in the area. For processing of materials with gamma rays, underground installations seem to be preferred. Many experimental gamma-ray facilities utilize the "swimming pool" design to provide adequate protection. A total dose over 300 roentgens may be fatal.

The thickness of shielding for monoenergetic x-rays and gamma rays may be estimated from the formula $\underline{I} = \underline{I}_0 \, e_{exp} \, (- \mu \underline{T})$, where $\underline{I}_0$ = the original intensity, $\underline{I}$ = the intensity after filtration or absorption, μ = linear absorption coefficient, and $\underline{T}$ = thickness of the absorber. On applying this equation using μ = 0.790 per centimeter for lead we find that to reduce the gamma ray intensity to 10% of the original intensity we need 2.92 centimeters lead. This equation is applicable not only to shielding problems but also to problems of radioactive decay and reactor neutron flux change as a function of reactor. High velocity electrons are far less penetrating than the gamma rays, and therefore they do not require as much shielding. This is of economic importance for an industrial application for high voltage electrons. For a 500-kilovolt electron accelerator it is suggested by the High Voltage Engineering Corp. that concrete walls 32 inches thick be used for shielding. The General Electric Company studies indicate that 18 to 24 inches of concrete is adequate to absorb all primary and subsequent secondary rays produced by a 1-Mev. unit. A maze-type entrance is recommended for entrance to a facility. Access doors may be made of 2-inch thick lead. The reason for these thicknesses is the development of lethal x-rays when the beam of high voltage electrons impinges on different materials.

PROCESSING TECHNIQUES

Careful consideration should be made of the penetrating nature of high voltage electrons and gamma rays in order to utilize them efficiently. As mentioned previously, gamma irradiation may be preferred for bulk materials. In the case of paper this would suggest irradiation in the form of rolls, skids, or ream-sized packages. On the other hand, the electron accelerators lend themselves ideally to a paper web treatment. Here again, however, it is important to notice that as in Fig. 9 which is a graph of the ionization intensity as a function of the penetration for one-sided irradiation we note a somewhat parabolic-shaped curve. It should be noticed that the dose is not uniform at all depths. Dosage increases to a maximum at a point about 1/3 along the total range. At a depth of about 2/3 of the total range the relative dose is equal to that at the surface. This particular depth is characterized as "the equal entrance equal exit dosage."

Irradiation from both sides of a sheet material ("cross firing") as illustrated in Fig. 10 presents advantages in that the useful thickness for two-sided treatment is about 2.4 times that obtained for a single-side irradiation. This is because the dosages in the last third of the range of each of the opposed beams are additive. It is also possible in some cases to cause a product to be irradiated from one side and then on the second pass it would be irradiated from the reverse side. The same principle as irradiation from two sides then applies and the product thickness can be 2.4 times that of the product that could be irradiated with the same beam intensity from one side.

If the web is such that the over-all thickness cannot be altered by using multiple plys, then another technique involving the irradiation at an angle may be utilized. The optimum angle of inclination, θ, is related to product thickness and beam energy by the following expressions; for single-side

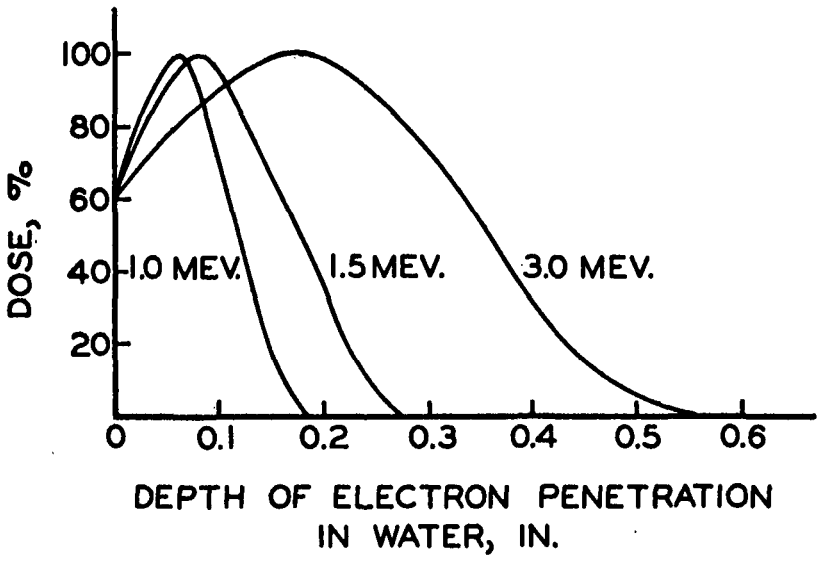

Figure 9. Dosage as a Function of Depth of Penetration for Irradiation from One Side

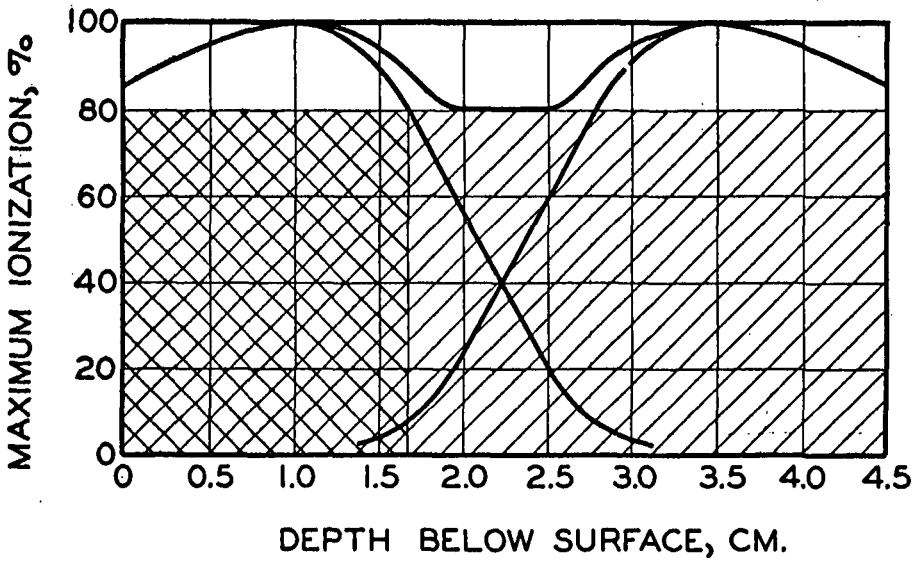

Figure 10. Dosage as a Function of Depth of Penetration for Irradiation from Two Sides

irradiation, $\cos \theta = \frac{T}{0.13}$ Mev.; for double-side irradiation, $\cos \theta = \frac{T}{0.31}$ Mev., where T is the product thickness in inches equivalent to unit gravity.

To obtain maximum efficiency and minimum cost in irradiation processing, it is necessary to select the conditions so that the maximum possible fraction of the electron beam power be absorbed in the product and that the radiation dosage be as nearly uniform as possible throughout the product.

If the thickness of the sheet of material being irradiated is much smaller than the range of the electron beam, efficiency can be achieved by causing the web to traverse back and forth underneath the irradiating head several times. This technique has been found very effective with the irradiation of plastic-coated wire.

A small percentage of the energy is absorbed in the window necessary to maintain the vacuum within the scanning head and the accelerator. The strength of titanium, nickel, and aluminum is adequate to withstand atmospheric pressure even in foils as thin as 0.005 of an inch or less.

Efficiency, in some cases, may be increased through the use of special filters to slow down the electrons. Although the filter will absorb a certain amount of energy, it is possible to increase the over-all absorption efficiency by developing a more even dose; and the efficiency of a double bombardment can be increased to more than 70% despite the added loss of the filter because the uniformity of the dose has been improved (3).

One of the first questions that may come to a person's mind is whether there is any hazard from radioactivity in the material that is being irradiated. At the electron voltages of possible commercial interest, there is no danger of radioactivity being retained in the product that has been irradiated. This

statement, of course, applies to irradiation of food materials, plastics, and fibrous materials based on cellulose.

Another question might be asked as to what voltage unit and what power unit is needed. The first answer, of course, is dependent on the thickness of material that needs to be irradiated and the stopping power of the material. In general, the lower the voltage of the facility, the lower the cost will be for the basic unit. The penetration will be largely dependent upon the density of the material, and a good average figure for penetration will be equal to 0.5 centimeter per Mev. (million electron volts).

Another consideration of prime importance is that of shielding. The higher the voltage of the accelerator, the greater should be the thickness of the shielding. A 500,000 electron volt unit will require about 32 inches of concrete or about 2 inches of lead metal.

Due to corona effects there is a considerable amount of ozone produced when operating an electron accelerator. Oxygen in the air is converted to ozone at the rate of 0.03 lb. per kwh. (kilowatt hour). An exhaust system should be installed which is capable of reducing the ozone level to 0.1 parts per million. The nature of the process may allow some latitude, depending upon the frequency with which personnel may be subjected to the ozonized atmosphere.

In designing a radiation facility it is well to avoid materials that tend to be degraded by radiation energy and materials that should be avoided include: wood, paper, many types of plastic (unless protected by metal), and many types of paints. Stainless steel, aluminum, and titanium would be recommended where corrosion is a problem; otherwise iron or steel for structural members would be satisfactory.

The design of the installation should be such that easy access without impairing the shielding requirements would be incorporated into the basic design. The maze-type installation would eliminate doors which would add considerably to the cost of the installation since they would need to be of thick lead.

Sufficient headroom should be provided for a direct path for the electrons and the accelerator tank. The I.C.T. (High Voltage Engineering) electron accelerators are equipped with cables and do not require as much headroom.

A closed circuit television installation would minimize problems of control of an irradiation facility. An ordinary television set could be used as the monitor.

The power of the unit should be such that it will handle the rate of production desired. The speed of a conveyor system likewise would need to be designed to match the power potential of the accelerator.

Safety controls are mandatory since lethal x-rays can be produced by a high-power electron beam on impinging materials.

APPLICATIONS

The patent literature is replete with schemes for using irradiation for a wide number of applications. They would be too numerous to mention individually in a report of this type, but range from such things as the scheme of irradiating food to prevent premature spoilage, or deinfestation of grain, which require very low dosages, to the vulcanization of rubber or cross-linking of polyethylene and other plastic materials which may require from 100 to 200 times as much energy (see Appendix). Table X lists some proposed applications and some that are already in commercial operation together with the dose in megarads and the power in pounds per kilowatt hour.

TABLE X

APPLICATIONS FOR IRRADIATION

Application	Dose, megarads	Lb./kwh.
Deinfestation of grain	0.025-0.1	10,000-30,000
Food preservation	0.1-5.0	200-8,000
Graft polymerization	1-2	400-800
Sterilization – drugs and medical supplies	2-3	250-400
Polyester curing	5-10	80-160
Silicone vulcanization	5-15	50-160
Rubber vulcanization	10-40	20-80
Cross linking of polyethylene	20-60	10-40

Although the paper industry as a whole has had very little inclination to get into the manufacture of chemicals, there seems to be a definite trend in this direction; and therefore mention of some of the possibilities for the processing of chemicals may be in order. As has been mentioned previously, a radiation process for ethyl bromide has been brought into successful operation by the Dow Chemical Company and the Standard Oil Company of New Jersey has developed a radiation process for sulfoxidation of alkanes. The radiation chemical processing of pulping by-products would appear to be a fruitful field for future studies.

The use of radiation chemistry in other papermaking areas such as sizing, coating, impregnation, lamination, flameproofing, cyanoethylation, changing the sensitivity of the fiber to water, oil, chemicals or dyes, etc. will undoubtedly be explored at some time or other.

COSTS OF RADIATION PROCESSING

COST OF NUCLIDE

The cost estimation for an undeveloped process is understandably an inexact operation full of frustrations. However, it may be well to try to develop some cost figures which will serve as orders of magnitude rather than precise estimates. The cost of an irradiation process is very strongly affected by the efficiency of the process. Unfortunately, this cannot be established with any great exactness for processes involving untried polymerizable or cross-linkable materials. Further studies on polymerization or cross linking of high G value materials would be very beneficial.

As a first approach we may wish to refer to the estimates made for gamma radiation processing costs as discussed by L. E. Kukacka and D. Manowitz (50). In discussing the cost of a gamma ray installation one of the first items encountered is the cost of the source. The Atomic Energy Commission has recently established the price schedule for Co^{60} as shown in Table XI. This table also includes some unofficial projected prices for Co^{60} when applied to large quantity orders. The cost of Cs^{137} has been set at $1.50 per curie for encapsulated material through June, 1966 and $1.02 per curie thereafter. This is under the jurisdiction of the Hanford Atomic Products Operation.

COSTS OF TRANSPORTATION

The cost of transportation may be estimated at 1 cent per curie per 1,000 miles for a maximum shipment of 100,000 curies Co^{60}. A 7-ton shipping cask will handle 125,000 curies Co^{60}. The cost of transportation includes freight charges, use of shipping containers, insurance, and carrier burden.

TABLE XI

ATOMIC ENERGY COMMISSION Co^{60} COST FIGURES

A. Small Quantities

Specific Activity in Curies per Gram	Price in Dollars Per Curie
1 thru 25	$ 2.00
26 thru 40	3.00
41 thru 55	4.00
56 thru 70	5.25
71 thru 85	5.65
86 thru 100	5.85
101 thru 115	6.05
116 thru 130	6.20
131 thru 145	6.40
146 thru 160	6.60
161 thru 175	6.80
176 thru 190	7.00
191 thru 205	7.20

B. Large Quantities [projected prices for Co^{60} (unofficial)]

15 thru 30	0.60
30 thru 100	0.30
100 thru 200	0.15
200 and over	0.11

Note: The above costs do not include transportation.

OPERATING COSTS

As in many other processes, the labor requirements for a radiation facility will depend on the design of the irradiator, and how it is integrated into the total process. A range of 0.1 to 1.5% of plant investment has been suggested for estimating operating costs for maintenance and utilities.

INSURANCE AND TAXES

It is estimated that the property insurance may be between 0.2 to 0.7% of the plant investment. Liability and indemnity insurance, together, represent an additional 0.2 to 0.73% of the total plant investment.

The state and local taxes may be estimated at 3 to 3.5% of the plant investment.

REPLENISHMENT COSTS

The annual replenishment costs for Co^{60} to maintain at least 90% of design strength is estimated at 12.5% of the original Co^{60} loading. For Cs^{137} this will be only 2.2% because of the longer half-life of Cs^{137}.

COST EXPERIENCE

For purposes of comparison we may wish to refer to the cost experience in building five different Co^{60} irradiation facilities, excluding the cost of the isotope. Each of these as listed in Table XII is concerned with food or medical product preservation.

A more useful cost estimate may be that for a Co^{60} facility for irradiating polyethylene film for shrink-film applications as given in Table XIII.

TABLE XII

ACTUAL COST OF FIVE Co^{60} FACILITIES

	Plant Number				
	I	II	III	IV	V
Facility cost, thousands dollars	489.4	695.0	1695.0	1731.7	1233.9
Breakdown, % of total cost					
Architectural and engineering service	24.2	12.24	16.35	25.00	20.8
Construction overhead	10.25	9.23	--	4.63	8.76
Construction (excluding pool and cell)	43.8	61.13	--	--	--
Storage pool	4.55	2.00	1.84	--	--
Radiation cell	17.10	15.40	10.87	--	20.3

(70.94; 70.37; 48.9)

TABLE XIII

POLYETHYLENE FILM IRRADIATION WITH Co^{60}

Total investment cost	$ 1,667,000
Cobalt 60 cost, cents/c	30
Source activity[a] (10^5c)	20.2
Radiation dose (10^5 rads)	200
Production rate, 10^6 lb./year	2.0
Unit cost, cents/lb.	
At 10% rate of return	34.4
At 25% rate of return	54.8
At 50% rate of return	95.0

[a] Source efficiency 21.5%.

In the above estimation, the initial nuclide charge is written off over the depreciation period. The rate of return is determined by the number of years of payoff. Thus, 50% is for a 1-year payoff.

COST OF AN ELECTRON ACCELERATOR FACILITY

The requirements for a paper application are such that specially designed electron accelerating equipment may be desirable. The thickness of paper or paperboard is sufficiently low to indicate relatively low voltages (200,000 to 750,000 volts). However, the flux density should be high to permit high-speed operation and maximum efficiency (greater efficiency is predicted for higher dose rates).

The "Glow-discharge Process," in its present form does not seem to fit the requirements for irradiation of paperboard. However, it is an interesting concept and bears study for possible paper coating and treatment applications.

The "insulating Core Transformer" type of electron source made by the High Voltage Engineering Corporation, the "Resonant Transformer Accelerator" made by General Electric Company, and the Dynamitron made by Radiation Dynamics Incorporated would appear to be the most suitable. Radiation Dynamics, Incorporated has made the following cost estimates:

Dynamitron accelerator voltage	1.5 Mev.
Accelerator putput	1.5 kw.
Depth efficiency	70%
Maximum product thickness for equal entrance-exit dose	0.190 inch
Maximum product output per megarad of radiation	8400 lb. per hour

Maximum area of product irradiated uniformly per megarad of radiation at 80% efficiency	4712 sq. ft./hr.
Conveyor rate for 1 megarad radiation dose (3 ft. wide web)	1571 sq. ft./hr.
Base costs	
Accelerator	$ 81,320
Facility (shielding, etc.)	37,000
Total	118,320
Annual costs (5-year amortization)	
Accelerator	16,264
Facility	7,400
Operating (1-man)	12,000
Overhead on operator	12,000
Utilities at 1.5 cents per kwh.	1,800
Maintenance contract	8,000
Total	59,464
Hourly costs (4,000 hours per year)	$ 14.86
Unit costs (costs per square foot)	3.16

Note: Assuming 5-year amortization. One operator, 2 shifts or 16 hours per day.

SUMMARY AND CONCLUSIONS

It is surprising that so little has been achieved in the application of irradiation to commercial processes despite the fact that radiation techniques seem to offer so many obvious advantages.

In a general sense, high-energy radiation can be considered as an excellent means of producing radicals and ions in a controlled manner within the bulk of a wide range of materials. It is possible in many cases to do the same by using chemical catalysts and heat. As new catalysts are being developed, the time required for a given reaction is lowered. We now have epoxy resins that can be cured in seconds, if desired. The catalyst or the curing agent is usually an amine of some type. With acidic catalysts the epoxy polymerization required higher temperatures and longer periods of time. The polymerization of polyester resins is catalyzed with various peroxy compounds. Cures can be accomplished at room temperature in both cases. These would represent the opposition a proposal for considering the use of irradiation would have to face.

The real advantages for radiation techniques seem to be in the ability to initiate reactions in solid materials, usually in a semifinished stage or in sterilization of heat-sensitive foods or pharmaceuticals or medical supplies. Radiation techniques are useful where contamination from a catalyst cannot be tolerated.

Radiation techniques are also valuable where instantaneous polymerization would be desirable as in the case of impregnated materials or in adhesive applications where a very rapid cure is desired.

The usefulness of irradiation techniques to the paper industry will be broadened as we gain more specific knowledge of the behavior of monomers

and polymerizable materials as required for a given application. Important areas appear to be studies of copolymerization using a monomer that is especially sensitive to irradiation in conjunction with a cheaper material, studies of free radical generating materials, studies of ways to make condensation reactions radiation sensitive, and studies of electrical applications involving specialized techniques to produce slow electrons which have been driven to the reaction site at high voltages.

Paper (or pulp) can be irradiated and be caused to store free radicals which even days later can cause graft polymerization to take place when the paper is impregnated with a suitable monomer. Such reactions can lead to fiber products with enhanced specific characteristics, be it resistance to water, chemicals, or fungus; improved wettability, flame resistance, or resistance to penetration by greases and oils. In other words, here we have another tool which may help broaden the general usefulness of paper products.

The choice of the type of facility would be predicated on the conclusions reached after a careful consideration of the nature of the process, the amount of money available for investment in a facility, and the required period for amortization. The two basic types are compared.

Type	Characteristics
Cobalt 60	1. Highly penetrating (43.2 cm. at 1 Mev.)
	2. Reliable
	3. Cannot be turned off – continuous (mechanical withdrawal)
	4. Gradual loss of activity
	5. Requires annual or semiannual replenishment
	6. Cost per delivered radiation dose is high
	7. Low dose rates
	8. Requires thick shielding

Type	Characteristics
High Energy Electrons	1. Low (but adequate) penetration
	2. Periodic maintenance required (metal windows must be replaced)
	3. Can be turned on or off
	4. Intensity does not change with age
	5. Low cost per delivered dose
	6. High dose rates possible
	7. Less shielding is required

LITERATURE CITED

1. Burrill, E. Alfred, Nondestructive Testing May-June, 1961:167-76.

2. The Engineer (Great Britain), Jan., 1960:8, 15 and 22.

3. Kircher, John F., and Jeffrey, David A., Battelle Tech. Rev. 14, 1:3-9(Jan., 1965).

4. Cooper, Daniel, ed. International Science and Technology 27:22-34(March, 1964).

5. Boehm, George A. W., Fortune LXX, no. 6:141-3, 152, 154, 158(Dec., 1964).

6. Chem. Eng. News 41:80-91(April 22, 1963).

7. Bolt, Robert A., and Carroll, James G., eds. Radiation effects on organic materials. New York, Academic Press, 1963.

8. Bovey, Frank A. The effects of ionizing radiation on natural and synthetic high polymers. New York, Interscience, 1958.

9. Charlesby, A. Atomic radiation and polymers. New York, Pergamon Press, 1960.

10. Chapiro, Adolph. Radiation chemistry of polymeric systems. New York, John Wiley and Sons, 1962.

11. Swallow, A. J. Radiation chemistry and organic compounds. New York, Pergamon Press, 1960.

12. Goodman, Jerome. Assigned to Radiation Research, Inc. U.S. pat. 2,932,591 (April 12, 1960).

13. Coleman, John H. Assigned to Radiation Research, Inc. U.S. pat. 3,068,510 (Dec. 18, 1962).

14. Coleman, John H. Assigned to Radiation Research, Inc. U.S. pat. 3,069,283 (Dec. 18, 1962).

15. Arthur, Jett C., Jr., Blouin, Florine A., and Dewint, Robert J., Am. Dyestuff Reptr. 49, no. 11:21-6(May 30, 1960); A.B.I.P.C. 31:177.

16. Bernard, Oliver R., Gagnaire, Didier, and Servoz-Gavin, Pierre. J. Chim. Phys. 60:1348-54(1963); C.A. 60:12220.

17. Liick, Haus, and Dell, Friedrick, Chimia (Aarau) 17, no. 1:1-8(1963); A.B.I.P.C. 34:204.

18. Florin, Roland E., and Wall, Leo A., J. Polymer Sci. 1A, no. 4:1163-73(April, 1963); A.B.I.P.C. 33:1976.

19. Horio, Masao, Imamura, Rikizo, and Muzukarni, Hideya, Bull. Inst. Chem. Res. Kyoto Univ. 41, no. 1:17-38(1963).

20. Huang, R. Y.-M., Immergut, B., Immergut, E. H., and Rapson, W. H., J. Polymer Sci. 1A, no. 4:1257-70(April, 1963).

21. Usmanov, Kh. U., Aikhodzhaev, B. I., and Azizov, U., Tr. Tashkentsk. Kouf. po Mirnomu Ispol'z At. Energii, Akad. Nauk Uz. SSR 1:295-8(1961); C.A. 56:14507.

22. Usmanov, Kh. U., and Azizov, U., J. Polymer Sci. (Part C, Polymer Symposia), no. 4:579-87(1964).

23. Tabata, Yoneko, Shimozawa, Ryosuke, and Sobue, Hiroshi. J. Polymer Sci. 54: 201-8(1961); C.A. 56:3056.

24. Beush, I., and Kaplan, G., Vysokomolekul. Soedin. 5, no. 10:1580-4(1963); C.A. 60:5707.

25. Sobue, Hiroshi, and Tabata, Yoneko, J. Polymer Sci. 43:459-65(1960); C.A. 54: 17946.

26. Henglein, Arnin, and Schneider, Christel, Z. physik. Chem. (Frankfurt) 18: 56-73(1958); C.A. 55:2253.

27. Olesen, Henning H. Lind, Electronics 37, no. 32:61-71(Dec. 28, 1964).

28. Ikamura, S., Motoyama, T., Manabe, T., and Inagaki, H. Large radiation source in industry. Large Radiation Sources in Ind., Proc. Conf., Warsaw. 1959. no. 1:361-73(1960); C.A. 55:12918.

29. Dolmatov, S. A., and Polak, L. S., Neflekhimeya 3, no. 5:683-9(1963); C.A. 60: 3102.

30. Figuet-Fayard, Florence, J. chim. phys. 56:692-8(1959); C.A. 54:2903.

31. Okamura, Seizo, Hayashi, Koichiro, Yamamoto, Masao, and Nakamura, Yoko, J. Chem. Soc. Japan, Ind. Chem. Sect. 65:728-31(1962); C.A. 57:15320.

32. Degering, Ed F., Calderella, G. J., and Maucini, M., U.S. Dept. Com., Office Tech. Serv. PB Report 145,895:40 p. (1959); C.A. 56:4923.

33. Balatine, D. S., Glines, A., Metz, D. J., Behr, J., Mesrobian, R. B., and Restaino, A. J., J. Polymer Sci. 19:219-24(1956); C.A. 52:9785.

34. Dalton, F. L., Houlton, M. R., and Sykes, J. A., Nature 200, no. 4909:812-14 (Nov. 30, 1963); A.B.I.P.C. 34:1614.

35. Golub, Morton A., J. Am. Chem. Soc. 80:1794-8(1958); C.A. 52:12571.

36. Barnes, W., Dewhurst, H. A., Kilb, R. W., and St. Pierre, L. E., J. Polymer Sci. 36:525-6(1959); C.A. 53:23065.

37. Williams, T. F., and Dole, Malcolm, J. Am. Chem. Soc. 81:2919-26(1959); C.A. 53:23057.

38. Kawai, Rinjiro, Kawamatsu, Shunji, Maeda, Yo, Harada, Minoru, Ueyama, Mamoru, and Hirai, Tadaaki, Chem. of High Polymers 15:523-30(1958); C.A. 54:11547.

39. Kotliar, Abraham M., J. Appl. Polymer Sci. 2, no. 5:134-42(1959); C.A. 54: 10469.

40. Charlesby, A., and Davidson, W. H. T., Chem. and Ind. (London) 1957:232-3; C.A. 51:9205.

41. Charlesby, A., Von Arnin, E., and Callaghan, L., Intern. J. Appl. Radiation and Isotopes 3:226-31(1958); C.A. 53:899.

42. Shinohara, Kenichi, and Takamatsu, Toshiaki. Sci. Papers Phys. Chem. Research (Tokyo) 53:29-35(1959); C.A. 54:16132.

43. Matsumoto, Akira, Chem. of High Polymers 20, no. 216:268-74(1963); C.A. 61: 5803.

44. Huang, R.Y.-M., and Rapson, W. J., J. Polymer Sci. (Part C, Polymer Symposia), no. 2:169-87, discn.:188(1963); A.B.I.P.C. 34:473.

45. Burke, Evelyn S., PB Rept. 140265:20 p.; C.A. 54:17878.

46. Stannett, Vivian, Tappi 47, no. 3:58A, 64A, 72A(March, 1964); A.B.I.P.C. 34: 1449.

47. Usmanov, Kh. U., Aikhodzhaev, B. I., and Azizov, U. Meshdunerod. Sympozium po Makroml. Khim. Doklady Moscow 1960 Sektsija 3:344-51.

48. Hillend, W. Jack. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1963. 73 p.

49. Snell, John. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1964.

50. Kukacka, L. E., and Manowitz, B., Nucleonics 23, no. 1:74-8(Jan., 1965).

APPENDIX

LIST OF PATENTS ON PROCESSES AND MANUFACTURE OF NEW PRODUCTS

U. S. Patents

Number	Issue Date	Assignee or Author	Title
1,169,571	1/25/16	H. Rosenthal	Art of coloring glass
1,818,073	8/11/31	Lehigh-Archer Daniels-Goodrich	Process of treating oils and products thereof
1,906,402	5/2/33	B.F. Goodrich	Vulcanizing rubber
2,457,203	12/28/48	Electronized Chemicals Corp.	Method of making scenting essential oils from plants
2,498,735	2/28/50	Electronized Chemicals Corp.	Electronic aging of alcoholic beverages
2,534,222	12/19/50	Electronized Chemicals Corp.	Methods of detoxifying poisonous compounds
2,668,113	2/2/54	United Shoe	Ahesive bonding process
2,670,483	3/2/54	J. J. Brophy	Stiffening portion of shoes
2,743,233	4/24/56	USA-AEC	Organic compound bond rupturing process
2,746,193	5/22/56	H. Lonnman	Decorating glassware by high energy irradiation
2,766,220	10/9/56	General Electric	Irradiation of octamethyl cyclotetra-siloxane & products thereof
2,793,970	5/28/57	M. R. Jenson	Method of manufacturing electrical capacitors
2,803,598	8/20/57	Esso Rsch. & Eng.	Gamma ray polymerization of unsaturated esters
2,803,599	8/20/57	Esso Rsch. & Eng.	Gamma ray polymerization of unsaturated nitrogen compounds
2,805,072	9/3/57	U.S. Rubber	Method of toughening golf ball covers
2,836,553	5/27/58	Esso Rsch. & Eng.	Irradiated resins
2,855,517	10/7/58	W.R. Grace & Co.	Irradiation treatment of polyethylene
2,858,199	10/28/58	IT & T	Crystal production

Number	Issue Date	Assignee or Author	Title
2,858,259	10/28/58	General Electric	Electron Irradiation of preformed polyamide resin
2,862,862	12/2/58	USA-AEC	Formation by irradiation of an expanded cellular polymeric body
2,863,812	12/9/58	DuPont	Irradiation process
2,865,824	12/23/58	Allied Chem. Corp.	Production of polymers of ethylenically unsaturated fluorine containing compounds
2,867,571	1/6/59	General Electric	Depolymerization of high molecular weight dextran
2,867,572	1/6/59	J.F. German and E.F. Degering	Deleading of gasoline by irradiation
2,868,988	1/13/59	USA(W. Miller)	Method of reducing transient reverse current
2,877,500	3/17/59	W.R. Grace	Process for preparing transparent polyethylene
2,878,174	3/17/59	W.R. Grace	Polyethylene
2,887,445	5/19/59	Monsanto	Production of polyethylene
2,895,891	7/21/59	General Electric	Cellulosic materials
2,897,092	7/28/59	General Electric	Polyethylene
2,900,277	8/18/59	General Electric	Process of applying protective coatings by means of high energy electrons
2,904,392	9/15/59	Pomerantz, et al.	Method of packaging and treating articles
2,904,480	9/15/59	W.R. Grace	Polyethylene
2,904,481	9/15/59	General Electric	Solid state polymerization
2,904,483	9/15/59	R. B. Long and H.J. Hibshman	Hydrocarbon radiochemical reactions
2,904,484	9/15/59	R.W. Houston, R.B. Long, and B.L. Tarmy	Radiochemical reactions
2,904,485	9/15/59	B.L. Tarmy and R.B. Long	Radiochemical treatment of heavy oils

Number	Issue Date	Assignee or Author	Title
2,905,606	9/22/59	R.B. Long, H.J. Hibshman, J.P. Longwell, and R.W. Houston	Conversion of hydrocarbons in the presence of neutron radiation and a hydrogenation catalyst
2,905,607	9/22/59	R.B. Long, H.J. Hibshman, J.P. Longwell, and R.W. Houston	Conversion of hydrocarbons in the presence of neutron radiation and a cracking catalyst
2,905,608	9/22/59	Dow	Treatment of catalyst materials with high energy radiations
2,905,610	9/22/59	E.P. Wigner	Conducting hydrocarbon conversions in nuclear reactors
2,906,678	9/29/59	General Electric	Process of irradiating polyethylene at elevated temperatures
2,906,679	9/29/59	General Electric	Irradiated polyethylene
2,907,675	10/6/59	DuPont	Process of coating polymeric substrates
2,910,372	10/27/59	DuPont	Irradiated concrete compositions
2,910,723	11/3/59	Traver Investments Inc.	Treating non-adherent surfaces to render them adherent
2,911,533	11/3/59	A.C. Damask (U.S.A.)	Electron irradiation of solids
2,914,452	11/24/59	Esso Rsch. & Eng. Co.	Conversion of organic compounds by radiation
2,919,473	1/5/60	General Electric	Molding of polyethylene irradiated with high energy electrons
2,921,006	1/12/60	General Electric	Polymerization with high energy electrons
2,924,559	2/9/60	General Electric	Polyethylene blend
2,926,126	2/23/60	Rohm & Haas	Preparation of graft copolymers
2,929,744	3/22/60	General Electric	Irradiated polyethylene & products therefrom
2,933,441	4/19/60	Astra Inc.	Process of making rubber articles

Number	Issue Date	Assignee or Author	Title
2,934,481	4/26/60	Union Carbide	Promotion of chemical reactions
2,936,261	5/10/60	General Electric	Sealing irradiated polyethylene
2,936,271	5/10/60	Esso Rsch. & Eng. Co.	Irradiation of polymeric materials
2,936,272	5/10/60	Esso Rsch. & Eng. Co.	Bisphenols
2,936,275	5/10/60	Esso Rsch. & Eng. Co.	Radiochemical treatment of drying oils
2,940,869	6/14/60	DuPont	Process of adhering an organic compound to a shaped organic polymer
2,940,912	6/14/60	DuPont	Initiation of polymerization by pre-irradiated solid carboxylic acids, amides and nitriles
2,940,913	6/14/60	DuPont	Process for preparing carboxylic acids by irradiation
2,940,914	6/14/60	DuPont	Synthesis of carboxylic acids
2,940,951	6/14/60	Union Carbide	Metallo-ceramic preparations
2,941,934	6/21/60	H.D. Anspon and F.E. Pschorr	Polymerization by temperature-controlled irradiation
2,945,792	7/19/60	General Electric	Polyolefins
2,945,793	7/19/60	USA-AEC	Process for coloring diamonds
2,945,795	7/19/60	Congoleum-Nairn	Process for increasing the hardness of flexible resin sheets by irradiating same
2,947,675	8/2/60	Esso Rsch. & Eng. Co.	Styrene polymerization process
2,948,664	8/9/60	Dow	Method of making cellular polyethylene
2,948,665	8/9/60	Dow	Process for making cellular polyethylene articles
2,948,666	8/9/60	General Electric	Irradiation process
2,949,413	8/16/60	Dow	Process for purifying propylene oxide

Number	Issue Date	Assignee or Author	Title
2,951,022	8/30/60	H.M. Hartzband, B.L. Tarmy, and R.B. Long	Preparing lubricating oils using radiation
2,951,024	8/30/60	Bar Dal	Irradiation of linear aliphatic saturated polyesters
2,951,796	9/6/60	Union Carbide Corp.	Inorganic & organometal compositions
2,952,593	9/13/60	Dow	Method of stabilizing vinyl aromatic foam
2,952,594	9/13/60	Dow	Latent foaming vinyl aromatic polymer compositions and method of making same
2,952,595	9/13/60	U.S. Rubber	Treatment with ionizing radiation of polyethylene containing particulate filler reacted with vinyltriethoxy-silane
2,952,596	9/13/60	Standard Oil (Indiana)	Activation of metals for grignard type syntheses
2,952,597	9/13/60	DuPont	Process for synthesizing nitriles
2,954,334	9/27/60	C.E. Stoops and J.M. Day	High VI lubricating oil and process for preparing same
2,955,953	10/11/60	DuPont	Process of adhering an organic coating to a polymeric substrate
2,955,994	10/11/60	Esso Rsch. & Eng. Co.	Radiochemical preparation of ion-exchange resins and soil conditioners
2,955,995	10/11/60	Esso Rsch. & Eng. Co.	Solvents for radio-chemical polymer-ization reactions
2,955,997	10/11/60	USA-AEC	Irradiation method of converting organic compounds
2,956,899	10/18/60	DuPont	Process of forming graft polymers on a shaped polymeric organic substrate
2,956,904	10/18/60	Minnesota Mining & Manufacturing	Pressure-sensitive adhesive tapes
2,956,938	10/18/60	DuPont	Synthesis of amines

Number	Issue Date	Assignee or Author	Title
2,956,940	10/18/60	P.J. Lucchesi and C.E. Heath	Radiation isomerization
2,956,941	10/18/60	C.E. Heath and P.J. Lucchesi	Radiation isomerization process
2,957,814	10/25/60	DuPont	Process for modifying polymers & products thus obtained
2,958,637	11/1/60	V. Voorhees	Conversion of hydrocarbons
2,958,638	11/1/60	Esso Rsch. & Eng. Co.	Reaction container for carrying out radiation induced chemical reactions
2,959,529	11/8/60	R.B. Long, R.W. Houston, H.J. Hibshman, and J.P. Longwell	Neutron irradiated hydrocarbon conversion process
2,959,530	11/8/60	R.B. Long, P.J. Lucchesi, B.L. Tarmy, and C.L. Read	Radiochemical hydrogenation process
2,959,531	11/8/60	Phillips Petroleum	Solid resins from irradiated epoxidized liquid conjugated diene polymers
2,959,565	11/8/60	Dow	Graft copolymers of polyglycol esters of acrylate and methacrylates on superpolyamide structures
2,960,453	11/15/60	W.R. Grace	Process for treating plastics and products thereof
2,961,388	11/22/60	Monsanto	Dimerization of trichloroethylene
2,961,389	11/22/60	Monsanto	Process for modifying polymers and products obtained thereby
2,962,430	11/29/60	J.P. Longwell, P.J. Lucchesi, and R.B. Long	Catalytic hydrocarbon radiochemical conversion process
2,962,431	11/29/60	E.M. Gladrow	Activated carbon catalyst radiochemical hydrocarbon conversions
2,963,412	12/6/60	Union Oil Co. of California	Process for preparing ketene

Number	Issue Date	Assignee or Author	Title
2,963,747	12/13/60	Western Electric	Method of plastic encapsulation using irradiation
2,964,454	12/13/60	Swift & Company	Improvements in irradiation polymerization
2,964,455	12/13/60	DuPont	Electron irradiation of organic polyethers
2,964,456	12/13/60	Dow	Stable waxing emulsions
2,964,457	12/13/60	Phillips Petroleum	Silica reinforced rubber
2,964,458	12/13/60	Houilleres	Preparation of ethylene polymers
2,965,553	12/20/60	DuPont	Curing of high molecular weight polymers by irradiation
2,967,137	1/3/61	General Electric	Irradiation of nylon
2,967,138	1/3/61	Esso Rsch. & Eng. Co.	Butyl rubber compounded with radio-polymerized alkanes
2,973,309	2/28/61	Esso Rsch. & Eng. Co.	Stable butyl latices
2,974,094	3/7/61	Esso Rsch. & Eng. Co.	Radio-sulfochlorination of paraffins
2,978,395	4/4/61	Esso Rsch. & Eng. Co.	Gamma ray polymerization of styrene with unsaturated esters
2,978,396	4/4/61	Esso Rsch. & Eng. Co.	Radiation induced ethylene polymerization
2,978,397	4/4/61	C.E. Heath, Jr. and P.J. Lucchesi	Radioalkylation of normal paraffins
2,978,412	4/4/61	Esso Rsch. & Eng. Co.	Copolymers of phosphorus sulfides and unsaturated organic esters
2,979,445	4/11/61	California Research Corp.	Process for converting cis-ethylenic compounds to their trans-isomers
2,979,446	4/11/61	Phillips Petroleum	Polymerization process
2,979,447	4/11/61	Dow	Process for the preparation of graft copolymers

Number	Issue Date	Assignee or Author	Title
2,981,668	4/25/61	Electronized Chemicals Corp.	Method for improving the properties of polymerized materials
2,981,670	4/25/61	Phillips Petroleum	Irradiation of olefins and mixtures thereof with alcohols
2,982,706	5/2/61	Esso Rsch. & Eng. Co.	High unsaturation irradiated butyl rubber
2,983,657	5/9/61	Compagnie de Saint-Gobain	Manufacture of grafted polymers
2,984,608	5/16/61	Societe Anonyme dite: Nobel-Bozel	Preparation of grafted polymer compositions
2,988,493	6/13/61	DuPont	Irradiation synthesis of sulfonyl vinylamines
2,989,385	6/20/61	Bell Telephone	Process for ion bombarding and etching metal
2,989,451	6/20/61	General Electric	Irradiated polyethylene
2,989,452	6/20/61	Bar Dal	Irradiated polymers
2,992,173	7/11/61	S.L. Ruskin	Methods for hydrocarbon reforming and cracking
2,996,441	8/15/61	Esso Rsch. & Eng. Co.	Radiolytic polymerization of cyclo-pentadiene
2,997,170	8/22/61	W.R. Grace	Laminates
2,997,418	8/22/61	General Electric	Cold welding of organopolysiloxanes
2,997,419	8/22/61	General Electric	Cold welding of polyester resins
2,997,432	8/22/61	Phillips Petroleum	Dyeing of 1-olefin polymers
2,997,433	8/22/61	Standard Oil of Indiana	Preparation of tertiary butylated aromatic compounds
2,998,329	8/29/61	Dow	Modification of cellulosic articles
2,998,365	8/29/61	Industrial Distributors Ltd.	Treatment of diamonds
2,999,056	9/5/61	DuPont	Irradiation bonding of acidic compounds to shaped polymeric structures

Number	Issue Date	Assignee or Author	Title
3,001,880	9/26/61	Union Carbide	Flexible glass compositions
3,001,920	9/26/61	Olin Mathieson & Thiokol Chemical	Conversion of diborane
3,001,922	9/26/61	DuPont	Polymers
3,002,910	10/3/61	USA-AEC	Catalytic conversion of organic compounds using penetrating radiation
3,002,911	10/3/61	USA-AEC	Radiolysis of organic compounds in the adsorbed state
3,003,310	10/10/61	G. D'Alelio	Combustion process employing solid polymeric fuels containing oxidizing agents
3,003,938	10/10/61	Esso Rsch. & Eng. Co.	Radio-oxonation of olefins
3,004,908	10/17/61	R. Haszeldine	Treatment of fluorinated hydrocarbons
3,005,096	10/17/61	Bell Telephone	Irradiation of monoclinic glycine sulphate
3,005,760	10/24/61	USA-AEC	Method of opposing irradiation induced viscosity increase in employment of organic fluids
3,006,829	10/31/61	W.R. Grace	Process for treating linear polypropylene
3,006,830	10/31/61	Dow	Method for improving the dyeability of fiber-forming cellulose esters
3,006,831	10/31/61	Shell Oil	Radiation of asphalts
3,008,885	11/14/61	Nobel-Bozel	Preparation of grafted cellulose base copolymers
3,008,886	11/14/61	Plastonics	Producing polymerized materials by irradiation
3,008,918	11/14/61	Dow	Graft polymers of sulfonated acrylate & acrylol taurine monomers on acrylonitrile polymer substrates
3,012,001	12/5/61	U.S. Rubber	Composition of vinyl chloride polymer plus two unsaturated monomers

Number	Issue Date	Assignee or Author	Title
3,012,950	12/12/61	Dow	Process for polymerizing diolefins
3,013,957	12/19/61	Metropolitan Vickers Electric	High energy radiation method for production of foamed polymers
3,018,235	1/23/62	B.L. Tarmy and R.B. Long	Radiochemical hydrocarbon conversion process
3,018,236	1/23/62	Esso Rsch. & Eng. Co.	Radiation induced ethylene polymerization
3,022,237	2/20/62	C.E. Heath, Jr.	Radiation methylation of unsaturated hydrocarbons
3,022,264	2/20/62	Dow	Compositions comprising graft copolymer of N-vinyl lactam monomer on acrylonitrile polymer substrate and method of making same
3,022,265	2/20/62	Dow	Compositions comprising graft copolymers of certain aminated alkenyl aromatic monomers on acrylonitrile polymer substrates and method of making
3,022,543	2/27/62	W.R. Grace	Method of producing film having improved shrink energy
3,026,257	3/20/62	Dow	Method of adding HBr to vinylaryl compounds
3,026,292	3/20/62	Dow	N-vinyl-3-morpholinone-polyamide graft copolymer and method of preparing same
3,027,311	3/27/62	Phillips Petroleum	Method of radiation graft copolymerization of N-vinyl lactam monomers on acrylonitrile polymer substrate
3,027,312	3/27/62	Phillips Petroleum	Irradiation of tubular materials
3,030,288	4/17/62	Phillips Petroleum	Production of alkenylamines
3,034,974	5/15/62	General Foods	Polysaccharide extraction by irradiation
3,038,843	6/12/62	T.F. Douman	Distillation process and apparatus
3,042,652	7/3/62	DuPont	Elastomeric composition comprising a benzene-insoluble radiation cross-linked polymer

Number	Issue Date	Assignee or Author	Title
3,046,207	7/24/62	General Electric	Irradiation of organopolysiloxanes
3,046,208	7/24/62	C.E. Heath, and P.J. Lucchesi	Radiolysis of monoolefins with a sensitizer
3,046,210	7/24/62	General Foods	Preparation of gelatin from collagenous materials
3,046,270	7/24/62	General Foods	Method of extracting gelatin from collagen stock by irradiation
3,048,529	8/7/62	Standard Oil of Indiana	Fluidized catalyst regeneration
3,048,531	8/7/62	E.L. Stogryn, and P.A. Argabright	Radiochemical sulfonation reaction
3,049,507	8/14/62	Dow	Dyeable graft copolymers of vinyl lactam monomer on polyolefin substrate
3,049,508	8/14/62	Dow	Graft copolymers of nitrogen-containing monomers on polyolefin substrates
3,050,453	8/21/62	Shell Oil	Alkylation process
3,050,498	8/21/62	Dow	Graft copolymers of aminated acrylate and methacrylate monomers on acrylonitrile polymers and method of preparing same
3,051,737	8/28/62	Council for Scientific & Industrial Research	Preparation and use of catalysts
3,053,742	9/11/62	U.S. Rubber	Irradiation crosslinking of polymers
3,055,815	9/25/62	British Insulated Callenders Cables	Polyethylene compositions
3,055,818	9/25/62	Esso Rsch. & Eng. Co.	Radiochemical conversion of hydrocarbons
3,056,171	10/2/62	Mimx Corp.	Inhibitor & thermal insulation liner for propellant grains
3,056,735	10/2/62	S-J Chemical	Method of adhering cured silicone rubber
3,057,790	10/9/62	DuPont	Selective hydrogenolysis

Number	Issue Date	Assignee or Author	Title
3,057,791	10/9/62	Phillips Petroleum	Radiation curing of polymers
3,058,899	10/16/62	Monsanto	Polymerization of vinyl compounds
3,058,950	10/16/62	Dow	Graft copolymer of N-vinyl-3-morpholine on polyolefin substrate and method of making same
3,061,483	10/30/62	USA-Sec. of the Army	Coating of metal with layers of titanium esters & a polymer by exposure to high energy radiation
3,061,530	10/30/62	American Enka	Treatment of articles formed from linear polymerization or polycondensation products
3,061,531	10/30/62	U.S. Rubber	Irradiation of vinyl chloride polymer plus two unsaturated monomers
3,062,729	11/6/62	Dow	Foamed articles of ethylene-propylene copolymers & method of making
3,062,812	11/6/62	American Chemical Co.	Process for production of cyclic ketoximes and lactams from cycloalkanes by means of ionizing radiation
3,065,157	11/20/62	DuPont	Process for modifying polymers & products thus obtained
3,065,158	11/20/62	Milton	Method of vulcanizing organosiloxanes
3,066,085	11/27/62	BX Plastics	Irradiation grafting of acrylonitrile on vinyl chloride-vinylidene chloride copolymers
3,067,115	12/4/62	W.H. Clingman, Jr.	Chemical conversions and reactions
3,068,122	12/11/62	Dow	Selected graft polymers & their preparation
3,071,524	1/1/63	Esso Rsch. & Eng. Co.	Reaction of olefins by radiation
3,072,548	1/8/63	Esso Rsch. & Eng. Co.	Hydrocarbon radiochemical conversion process
3,073,766	1/15/63	Esso Rsch. & Eng. Co.	Catalyst preparation

Number	Issue Date	Assignee or Author	Title
3,074,866	1/22/63	G. D'Alelio	Irradiated polymers
3,074,867	1/22/63	J.E. Shewmaker and J.F. Nelson	Irradiated petroleum resins
3,075,904	1/29/63	G. D'Alelio	Irradiated polymers
3,075,905	1/29/63	G. D'Alelio	Irradiated polymers
3,075,906	1/29/63	K.T. Chow	Process for irradiating pearls & product
3,076,843	2/5/63	DuPont	Fluorinated derivatives of carboxylic acid hydrazides
3,077,417	2/12/63	Dow	Stabilization of wood and wood-like products with acrylic-like compounds
3,077,418	2/13/63	Dow	Stabilization of wood & wood products with styrene, acrylonitrile, bis (2-chloroethyl) vinylate, phosphonate
3,077,419	2/12/63	Dow	Stabilization of wood & wood products with vinyl compounds
3,077,420	2/13/63	Dow	Stabilization of wood & wood products with epoxy compounds
3,079,312	2/26/63	DuPont	Shaped polymeric articles
3,080,306	3/5/63	Esso Rsch. & Eng. Co.	Irradiation of polymeric compounds
3,081,243	3/12/63	Armour	Method of making fluorinated compounds
3,082,161	3/19/63	G. D'Alelio	Irradiated polymers
3,084,114	4/2/63	General Electric	Irradiated filler-containing polyethylene
3,084,115	4/2/63	U.S. Rubber	Method of vulcanizing rubber
3,084,116	4/2/63	Phillips Petroleum	Production of thiols and sulfides using anion exchange resin and/or an epoxy compound
3,084,117	4/2/63	Union Oil	Organoclay-polyolefin composition
3,085,953	4/16/63	Monsanto	Dimerization of dichloroethylene

Number	Issue Date	Assignee or Author	Title
3,087,880	4/30/63	P. Kollsman	Method of making permselective membranes
3,088,896	5/7/63	Pennsalt	Oxidation of trifluoroethanol
3,090,735	5/21/63	USA-Sec. of Commerce	Method for making a fiber with reversible dimensional change
3,090,736	5/21/63	Dow	Insoluble polyacrylic acid salts & method of preparing same
3,090,738	5/21/63	Dow Corning	Method of curing organosilicon compounds
3,090,739	5/21/63	Toyo Rayon	Method of producing nitroso compounds or oximes
3,090,770	5/21/63	W.R. Grace	Blended polyethylene compositions of improved clarity and method of making same
3,092,563	6/4/63	Esso Rsch. & Eng. Co.	Polymerization process
3,093,560	6/11/63	Houilleres	Method of preparing polyformaldehyde material having improved characteristics
3,093,561	6/11/63	Phillips Petroleum	Reinforcement of rubber with irradiated carbon black
3,096,267	7/2/63	Kurashiki Rayon Co.	Radiation polymerization of vinyl acetate
3,099,611	7/30/63	Distillers Co., Ltd.	Polyethylene irradiation process
3,100,182	8/6/63	Gulf	Irradiation destruction of complexes
3,100,184	8/6/63	USA-AEC	Tritium production by neutron irradiation of aluminum-lithium alloys
3,100,185	8/6/63	Gulf	Method of improving wear properties of a mineral and fatty oil lubricant mixture by irradiation
3,101,275	8/20/63	DuPont	Process of coating a shaped swollen polymer substrate & treating with ionizing radiation
3,101,276	8/20/63	DuPont	Process for grafting polymers to cellulose substrates

Number	Issue Date	Assignee or Author	Title
3,101,306	8/20/63	Saint-Gobain	Reticulated polyvinyl chloride & method of making same
3,102,087	8/27/63	Saint-Gobain	Polymerization by gamma rays & novel products produced thereby
3,104,214	9/17/63	DalMon Research Co.	Irradiated polymers
3,104,216	9/17/63	Union Carbide	Irradiation of metal oxides
3,104,983	9/24/63	IBM	Method of curing magnetic tape binder comprising butadiene acrylonitrile and phenolic resin with subatomic radiation
3,105,024	9/24/63	Esso Rsch. & Eng. Co.	Catalytic olefin polymerization method
3,105,801	10/1/63	Shell Oil	Process for polymerizing unsaturated aldehydes using ionizing radiation and resulting polymers
3,105,802	10/1/63	Phillips Petroleum	Synthesis of fatty acids

British Patents

552,388	4/6/43	Hatfield	An improved method of and means for coating the surface of solid bodies
665,262	1/23/52	Electronized Chemicals Corp.	Improvements in methods of polymerizing or condensing chemical substances
665,263	1/23/52	Electronized Chemicals Corp.	Method of treating and transforming chemical substances
714,843	9/1/54	Imperial Chemical Industries Ltd.	Process for the manufacture of ethylene polymers & the inter polymers
730,476	5/25/55	UK-AEA	Improvements in or relating to polymeric substances
732,047	6/15/55	UK-AEA	Improvements in or relating to treatment of polymeric substances
732,973	7/6/55	British Insulated Callender's Cables Inc.	Improvements in the manufacture of electric cables having oil impregnated insulation

Number	Issue Date	Assignee or Author	Title
739,709	11/2/55	UK-AEA	Improvements in or relating to polymeric substances
740,899	11/23/55	UK-AEA	Improvements in or relating to polymeric substances
741,826	12/14/55	UK-AEA	Improvements in or relating to polymeric substances
742,933	1/4/56	UK-AEA	Improvements in or relating to polymeric substances
747,478	1/4/56	UK-AEA	Improvements in or relating to polymeric substances
749,680	5/30/56	UK-AEA	Treatment of polymeric substances
761,766	11/21/56	UK-AEA	Treatment of polymeric substances
762,953	12/5/56	General Electric	Polymerization of organic compounds with high energy electrons
766,802	1/23/57	British Insulated Callender's Cables Ltd.	Improvements in the manufacture of electric cables and insulated wire
768,666	2/20/57	Monsanto	Improvements relating to the production of polymeric materials
768,670	2/20/57	Monsanto	Improvements relating to the production of polymeric materials
770,594	3/20/57	Hercules Powder Co.	Improvements in or relating to use of nuclear fission in synthesizing organic compounds
773,529	4/24/57	General Electric	Improvements in the treatment of polymeric materials
774,161	5/8/57	General Electric	Improvements relating to the treatment of polyethylene
775,874	5/29/57	General Electric	Bombardment of rubbers with high-energy electrons
781,421	8/21/57	Monsanto	Production of polymers of ethylene
782,442	9/4/57	British Insulated Callender's Cables, Ltd.	Improvements in manufacture of electric cables

Number	Issue Date	Assignee or Author	Title
784,037	10/2/57	General Electric	Improvements in polyethylene and articles therefrom
784,161	10/2/57	British Insulated Callender's Cables, Ltd.	Improvements in electric cables and insulated wires
784,274	10/9/57	Barb and Yarsley	Radiation-induced polymerization
784,624	10/9/57	Esso Rsch. & Eng. Co.	Radioactive polymerization of styrene with unsaturated esters
784,923	10/16/57	Badische Anilin & Soda Fabrik	Process for improving the properties of shaped articles of film-forming polyethylene
785,505	10/30/57	General Electric	Improvements relating to irradiated polyethylene
785,611	10/30/57	Esso Rsch. Eng. Co.	Improvements in or relating to chemical reactions
792,345	3/26/58	British Insulated Callender's Cables, Ltd.	Improvements in the manufacture of composite articles
798,146	7/16/58	General Electric	A method of producing cross-linked polyvinyl alcohol
798,980	7/30/58	U.S. Rubber	Improvements in golf balls
800,563	8/27/58	Dow	Treatment of catalyst materials
801,528	9/17/58	Centre national de la recherche scientifique	Graft polymers or copolymers
801,563	9/17/58	Foster Wheeler, Ltd.	Process for the dehydrogenation of hydrocarbons
802,552	10/8/58	Esso Rsch. & Eng. Co.	Reactions involving irradiation
802,620	10/8/58	E.I. DuPont	Improvements in or relating to the production of coatings
802,621	10/8/58	E.I. DuPont	Improvements in or relating to the production of coatings

Number	Issue Date	Assignee or Author	Title
805,818	12/10/58	General Electric	Process for irradiating flat stock organic polymers
805,819	12/10/58	General Electric	Process for irradiating flat stock organic polymers
805,897	12/17/58	T. I. (Group Services) Ltd.	Improvements relating to the manufacture of plastics
809,183	2/18/59	Siemens-Schuckert-werke	Process for influencing the molecular structure of plastics by irradiation
809,838	4/4/59	Centre Nationale de la Recherche Scientifique	Improvements in grafting polymers or copolymers
810,041	3/11/59	T. I. (Group Services) Ltd.	Improvements relating to the production of bodies of plastics
810,574	3/18/59	Esso Rsch. & Eng. Co.	Preparation of sulfonates
811,844	4/15/59	Steigerwald	Treatment of thermoplastic synthetics
811,847	4/15/59	Steigerwald	Production of substances of high molecular weight
811,903	4/15/59	Esso Rsch. & Eng. Co.	Curing films of butadiene-styrene copolymers
812,056	4/15/59	Industrial Distributors Ltd.	Treatment of diamonds
816,024	7/8/59	DuPont	Improvements in or relating to the production of coatings
816,230	7/8/59	Revertex, Ltd.	Improvements in the vulcanization of aqueous dispersions of rubber
816,791	7/22/59	Centre Nationale de la Recherche Scientifique	Improvements in method of cross-linking or vulcanizing synthetic resins by means of ionizing radiations
818,919	8/26/59	Esso Rsch. & Eng. Co.	Irradiation of polymers and copolymers of isobutylene
819,147	8/26/59	Esso Rsch. & Eng. Co.	Irradiation of polyolefins to control their molecular weight

Number	Issue Date	Assignee or Author	Title
819,451	9/2/59	Esso Rsch. & Eng. Co.	Polymerization of olefins
819,810	9/9/59	General Electric	Method of increasing the solvent resistance of polyethylene
820,120	9/16/59	DuPont	Process for modifying the structure and properties of addition polymers
820,121	9/16/59	Tube Investments Ltd.	Method of lining pipes & vessels
820,168	9/16/59	General Electric Co.	Improvements relating to irradiated filler-containing polyethylene
822,425	10/28/59	Dow	Process for making cellular polyethylene articles
822,632	10/28/59	Esso Rsch. & Eng. Co.	Lubricating oil compositions
822,751	10/28/59	Monsanto Chem. Ltd.	Polymerization process
823,462	11/11/59	Union Carbide Corp.	Improvements in the preparation of graft copolymers
825,945	12/23/59	General Electric Co.	Sealing irradiated polyethylene sheet material
827,350	2/3/60	Esso Rsch. & Eng. Co.	Radio-oxonation of olefins
828,717	2/24/60	T.I. (Group Services) Ltd.	Improvements relating to the curing of plastics
828,739	2/24/60	British Insulated Callender's Cables Ltd.	An improved method of making cellular polyethylene
829,512	3/2/60	Dow	Method for cross-linking vinyl chloride polymers
830,515	3/16/60	St. Gobain	Improvements in or relating to methods of polymerization using gamma radiation
830,820	3/23/60	DuPont	Improved process for viscose production

Number	Issue Date	Assignee or Author	Title
830,899	3/23/60	General Electric Co.	Improved irradiated polyethylene
831,150	3/23/60	T.I. (Group Services) Ltd.	Improvements relating to the chlorination of polymers
831,197	3/23/60	T.I. (Group Services) Ltd.	Improvements relating to latex
831,257	3/23/60	General Electric Co.	Stable irradiated polyethylene
831,319	3/30/60	Esso Rsch. & Eng. Co.	Radiolytic polymerization of cyclopentadiene
831,833	4/6/60	Esso Rsch. & Eng. Co.	Preparation of stable butyl rubber latices
831,842	4/6/60	Esso. Rsch. & Eng. Co.	Improved irradiated resins
831,896	4/6/60	Phillips Petroleum	Improvements in irradiated olefin polymers
831,914	4/6/60	General Electric Co.	Improvements in irradiation process
832,484	4/13/60	Union Carbide	Improvements in or relating to irradiation of metal alloys
832,746	4/13/60	Union Carbide	Improvements in or relating to irradiation of starch
832,747	4/13/60	Union Carbide	Process for carrying out oxidation-reduction reactions
833,594	4/27/60	Monsanto Chem. Co.	Chlorination of alkyl esters of aromatic carboxylic acids
833,610	4/27/60	U.S. Rubber	Improvements in vinyl chloride polymer compositions
834,536	5/11/60	W.T. Henley's Telegraph Works Co., Ltd.	Improvements in or relating to gas-filled electric cables
835,120	5/18/60	T.I. (Group Services) Ltd.	Causing color changes in polymer plastics by irradiation

Number	Issue Date	Assignee or Author	Title
835,121	5/18/60	Monsanto Chem. Co.	Irradiation of chemical reagents in nuclear reactors
837,504	6/15/60	Dow	Method of making cellular polyethylene
840,070	7/6/60	Esso Rsch. & Eng. Co.	Irradiated polyethylene
842,277	7/27/60	Dow	Process for the catalyzed abnormal addition of hydrogen sulphide to unsaturated compounds
842,873	7/27/60	Sequoia Process Corp.	Radiation treatment of polyethylene
843,063	8/4/60	Dow Chemical Co.	Radiation graft copolymerization of N-vinyl lactam monomers on acrylonitrile-polymer substrates
844,231	8/10/60	Dow	Method for crosslinking polymers of hydrocarbon olefins
844,791	8/17/60	E.G.Cockbain, T.D. Pendle, and D.T. Turner	Polymer compositions
849,042	9/21/60	General Electric	Improvements relating to polyolefins
850,965	10/12/60	T.I. (Group Services) Ltd.	Improvements relating to the manufacture of expanded polymerization products
852,532	10/26/60	Houilleres	Preparation of ethylenic hydrocarbon polymers
852,613	10/26/60	U.S. Rubber Co.	Irradiation of polymers
852,949	11/2/60	Esso Rsch. & Eng. Co.	High molecular weight multipolymers and derivatives thereof
853,737	11/9/60	T.I. (Group Services) Ltd.	Irradiation of polymers
853,795	11/9/60	S.H. Pinner, and W.H.T. Davison	Low-temperature polymerization of olefinic monomers
853,970	11/16/60	Centre National de la Recherche Scientifique	Improvements in graft polymerization utilizing ionizing radiation

Number	Issue Date	Assignee or Author	Title
853,971	11/16/60	Centre National de la Recherche Scientifique	Improvements in graft polymerization using ionizing radiation as the graft polymerization initiator
855,213	11/30/60	Imperial Chemical Industries	A process for the production of vinyl chloride polymers
855,711	12/7/60	Rohm & Haas	Graft copolymers and preparation thereof
860,408	2/1/61	DuPont	Improvements in or relating to the modification of synthetic polymers
861,454	2/22/61	B.X. Plastics	Manufacture of new graft copolymers
861,455	2/22/61	B.X. Plastics	Manufacture of new graft copolymers
862,610	3/15/61	B.X. Plastics	Manufacture of new graft copolymers
862,865	3/15/61	Dow	Coated polyolefin
863,211	3/22/61	R.R. Smith	Graft copolymers
863,395	3/22/61	K. Stevens	Irradiated polyethylene
866,069	4/26/61	T.I. (Group Services) Ltd.	Improvements relating to the manufacture of plastics
866,819	5/3/61	W.R. Grace	Improvements in the treatment of polyethylene and like polyolefins
866,846	5/61	U.S. Rubber Co.	Irradiated vinyl chloride copolymers
868,304	5/17/61	Houilleres	Improvements in or relating to processes for the polymerization of ethylene
868,855	5/25/61	Houilleres	Improvements in or relating to methods for the production of polymers
870,052	1/25/57	R.R. Smith	Graft copolymers of cellulose triacetate and styrene
871,572	6/28/61	B.X. Plastics	Improvements in or relating to graft copolymers
871,586	6/28/61	Union Carbide	Improvements in and relating to polyethylenes

Number	Issue Date	Assignee or Author	Title
873,600	9/4/61	T.I. (Group Services) Ltd.	Process for preparation of vinyl polymers
876,660	4/27/60	Kurashiki Rayon Co., Ltd.	Polymerization of vinyl acetate with γ-ray irradiation
881,281	11/1/61	U.S. Rubber	Improvements in vulcanizing rubber
883,275	11/29/61	J.C. Barford and N.E. Davenport	Irradiated synthetic rubber-resin blends
883,473	11/29/61	Nobel-Bozel	Polymer emulsions by radiochemical grafting
884,999	12/20/61	W.H. Stafford, W.H. Taylor, and W. Miller	Polymerization of trans-1,2-dichloro-ethylene
887,440	1/17/62	Compagnie de Saint-Gobain	Cross-linked poly(vinyl chloride)
890,145	2/28/62	Soc. Anon. Ethylene Plastique	New Process for the preparation of novel copolymers
894,395	4/18/62	DuPont	Improvements relating to graft co-polymers of condensation polymers
894,753	4/26/62	Centre Nationale de la Recherche Scientifique	Process for making graft copolymers
895,478	5/2/62	Heberlein & Co., A.G.	Improvements in or relating to cellu-losic material
895,479	5/2/62	Heberlein & Co., A.G.	Improvements in or relating to cellu-losic material
899,683	6/27/62	Nobel-Bozel	Improvements in or relating to polymer irradiation
900,571	7/11/62	J.A. Snelgrove	High-molecular-weight poly(vinyl acetates) and poly(vinyl alcohols)
906,324	9/19/62	Heberlein	Improvements in or relating to cellu-losic textiles
907,688	10/10/62	T.I. (Group Services) Ltd.	Improvements in or relating to the production of cured coatings of poly-meric material

Number	Issue Date	Assignee or Author	Title
909,061	10/24/62	R.W. Pearson	Urethan promoters of radiation curing of polymers
917,437	2/6/63	Heberlein & Co., A.G.	Improvements in or relating to the treatment of cellulosic material
925,465	8/8/63	Heberlein & Co., A.G.	Improvements in or relating to the treatment of cellulosic material
929,204	6/19/63	Heberlein & Co., A.G.	Improvements in or relating to the treatment of cellulose film
929,741	6/26/63	Heberlein & Co., A.G.	Improvements in or relating to the finishing of cellulosic textile materials
930,427	7/3/63	Heberlein & Co., A.G.	Improvements in or relating to the finishing of cellulosic textile material
941,689	11/13/63	Heberlein & Co., A.G.	Improvements in or relating to cellulosic textile materials
945,701	1/8/64	Shell Internationale Research Maatschappij N.V.	Vinyl polymerization of high-energy irradiation

Canadian Patents

545,645	9/3/57	L.G. Brazier	Manufacture of electric cables
648,898	9/18/62	A.J. Restaino, and W.N. Reed	Process of producing graft copolymers
667,686	7/30/63	G. Heberlein, and F. Munzel	Cellulosic films
672,778	10/22/63	F. Munzel	Cellulosic textile finishing process and product
678,034	1/14/64	R.C. Sovish, and F.L. Saunders	Modification of cellulosic articles

Number	Issue Date	Assignee or Author	Title
		French Patents	
Addn. 74,130	3/3/61	J. Durup, and M. Magat	Graft copolymers
982,463	6/11/51	J. Doucerain	Polymers
1,147,722	11/28/57	J. Gabilly, and M. Jobard	Grafted vinyl polymers
1,151,359	1/29/58	J. Leprevost, and P. Cacheux	Polymerization and polycondensation of plastic material
1,160,106-8	7/8/58	Houilleres du Bassin-du-Nord et du Pas-de-Calais	Graft copolymers
1,166,793	11/14/58	C. Wippler	Improving mixtures of polymers by irradiation
1,170,326	1/13/59	C. Lumbroso, H. Sack, and G. Stroh	Polyethylene-base graft copolymers
1,171,117	1/22/59	C. Wippler	Cross-linked poly(vinyl chloride)
1,187,214	9/8/59	C. Wippler	Cross-linking of vinyl chloride polymers and copolymers
1,198,188	12/4/59	C. Wippler	Vinylcarbazole copolymers
1,210,101	3/7/60	Nobel-Bozel	Irradiation of polymers which can be grafted
1,210,632	3/9/60	Houilleres du Bassin-du-Nord et du Pas-de-Calais	Polymers for films and coatings
1,210,637	3/9/60	L. Adany	Grafting of vinyl monomers onto paraffinic hydrocarbons by using radiation
1,241,211	12/12/60	Compagnie francaise de raffinage	Polymerization of conjugated diolefins
1,279,089	11/6/61	Heberlein & Co. A.G.	Method for reducing the swelling and increasing the dimensional stability of sheet materials containing cellulose, especially regenerated cellulose, and resulting products

Number	Issue Date	Assignee or Author	Title
1,288,829	3/30/62	C. Wippler, and R. Gautron	Radiochemical grafting onto poly(vinyl chloride)
1,300,770	7/2/62	Dow Chemical Co.	Process for modifying articles such as cellulosic films, fibers, and fabrics
1,334,305	8/9/63	Ethylene-Plastique S.A.	Radiochemical grafting of polymers
1,337,235	9/13/63	Compagnie Francaise de Raffinage	Irradiation polymerization of ethylene

German Patents

1,023,221	1/23/58	W.V. Smith	Polyethylene with improved mechanical and thermal properties
1,024,240	2/13/58	K. Graham, and S. Gluckman	Graft copolymerization by irradiation
1,047,433	12/24/58	W.H. Yanio, and J.D. Calfee	Polymerization of 1-chloro-1-fluoro-ethylene or its mixtures with vinyl chloride by irradiation
1,075,826	2/18/60	E.J. Lawton	Irradiation of polyamides
1,084,233	6/30/60	D. Tanner	Irradiation of natural polymers
1,085,666	4/11/56	E.J. Lawton	Irradiation of polyethylene
1,086,047	7/28/60	A. Chapiro, M. Magat, and J. Sebban-Danon	Graft polymer preparation by irradiation
1,086,429	8/4/60	E.J. Lawton	Continuous irradiation of polymers
1,113,677	10/7/59	G. Heberlein, and F. Muenzel	Improving the mechanical properties of textiles from natural or artificial cellulose-containing fibers

Number	Issue Date	Assignee or Author	Title
		Japanese Patents	
6675	1961	K. Shinohara, A. Amemiya, and E. Maeda	Improving the surface of polyethylene by treating with ionizing radiation
9598	1961	I. Sakurada, N. Okada, and Y. Akiyama	Prevention of decomposition of cellulose by ionizing radiation
9837	7/31/62	T. Hirayama, T. Mogi, and S. Kobayashi	Graft copolymerization of polyethylene with styrene
9992	1961	I. Sakurai, and N. Okada	Graft copolymerization of poly(vinyl alcohol) by radioactive rays
13,936	1961	I. Sakurada, S. Okamura, H. Inagaki, K. Yagi, and S. Saheki	Emulsification polymerization of cationic vinyl resins by irradiation
13,938	1961	Y. Hosaka, M. Takehisa, Y. Urano, and M. Yasumoto	Irradiation polymerization of ethylene
14,041	1961	T. Haneda, M. Ishihara, and Y. Yamane	Solution of polyacrylonitrile
		U.S.S.R. Patents	
116,349	1/19/59	V.V. Korshak, S.R. Rafikov, V.A. Sergeev, and P.L. Tsetlin	Radiation in polymerization of monomers
138,043	6/21/60	S.S. Leshchenko, E.E. Finkel, N.I. Sheverdina, L.V. Abramova, and V.L. Karpov	Thermal stabilization of polyethylene